

**J. M. EDER AND E. VALENTA:  
CONTRIBUTIONS TO PHOTOCHEMISTRY AND  
SPECTRAL ANALYSIS.**

**CONTRIBUTIONS TO**

**PHOTOCHEMISTRY**

**AND**

**SPECTRAL ANALYSIS**

**OF**

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**INCLUDES FIVE PIECES WITH 93 ILLUSTRATIONS IN TEXTS AND 60 TABLES**

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## PREFACE.

The present work contains a large number of studies on the Areas of photochemistry, sensitometry and spectral analysis, which are covered by a number of years at the k. k. Graphic teaching and research institute were executed and the results of which are in themselves devices for scientific and practical photography shut down. The works collected in this book were published in a period of carried out by the authors and their scientific collaborators for twenty years, what in connection with the fact that they extend to different areas, with it that a large part of the treatises were published very scattered at the time and thereby the overview of the organically interrelated treatises was very affected.

For this reason and because these investigations are currently of topical interest are likely to have, the same were in the present work, expanded by some supplementary, as yet unpublished work and through a new series of heliographic images of various spectrum photographs, combined into one whole.

It contains the photographic sensitizers for silver bromide plates, which for practical photography as well as for the objective representation of the spectral phenomena are so important, exhaustively treated and their application to three-color photography in connection with the spectral analytical properties of the preparations, Discussed photographs and pigment colors.

Scientific actinometry and sensitometry, chemical brightness more artificial Light sources, the study of the lightfastness of dyes, respectively whose color lacquers, which latter for the color technician who is practical with the The production of printing inks for graphic purposes is important, as is the investigation from printing inks to opacity etc. has been converted into experimental ones based on our own methods Treatment drawn.

Finally, our publications give a clear overview in this summary Picture of the performance of different earlier and more recent spectral analyticals Investigation methods with the prismatic spectrum (glass and mountain crystal) as well as with the diffraction spectrum. For the results of their spectral analysis Investigations which are contained in the memoranda of the Imperial Academy of Sciences were published, the authors were from the imperial academy of Awarded the Lieben Prize in 1895.

With the imprint of our wavelength measurements from different spectra together heliographic tables we comply with a request repeatedly addressed to us, since the small number of separata that were printed from these works has long been is exhausted and the comparison of those examined by us and in part by us discovered spectral phenomena in further. Research by many a spectrum analyst appears desirable.

The book and all the accompanying illustrations went to press on

II. Section (school for the book and illustration trade) of the k. k. Graphic teaching Research institute in Vienna.  
VIENNA in April 1904.

The writers.

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"Austrian: he Chemiker-Zeitung, Vienna.

«Photographische Correspondenz •, Vienna.

«Protocol of the III. International Congresses for Applied

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«Negotiations of the IV International Congress for Applied Chemistry », Berlin.

Meeting reports, memoranda and scoreboards of the Imperial Academy of Sciences in Vienna.

"Journal for physical chemistry", Leipzig.

Corrections.

On page 388 of Part I it is said in the table:

«III. Spark and arc spectrum of aluminum from). = 1899 to). = 1854 »instead of: bow spectrum K a y s er and Runge correctly called: Bogenspectrum Runge («Ann. D. Physics and Chemistry, 1895, Vol. LV, pag. 44); further is to note that Runge in the cited treatise the

Observation. an indistinct Al line on wavelength 1930 4 in the arc spectrum of aluminum.

On p. 50, Part II, footnote 3, instead of Part I., p. 52

III. Theil, p. 52.

On pag. 88, Part II, footnote 1, instead of Part I., p. 56

III. Theil, p. 56.

On p. 94, Part II, footnote 2, instead of Part I., p. 60

III. Theil, p. 60.

On page 95, Part II, footnote 3, instead of III. Theil, p. 37Part II, p. 37.

On pag. 126, Part II, footnote 2, instead of Part I., pag. 1

III. Part, p. 1.

On pag. 130, Part II, footnote 1, instead of Part II, pag. 128Part I, p. 128.

On pag. 134, Part II, footnote 1, instead of Part I., pag. 1

III. Part, p. 1.

I.

## SPECTRAL ANALYTICAL EXPLORATIONS.

About the visible and the ultraviolet Emission spectrum

faintly glowing more burning

Hydrocarbons (Swan's Spectrum) and the OxyHydrogen-Flame (water vapor spectrum).

Of

J. M. Eder.

(Presented at the session of the Imperial Academy of Sciences on May 8, 1890.)

Over the emission spectrum of weakly luminous hydrocarbons that burn in air or oxygen flames, as well as especially from the Bunsen's see luminous gas flame, refer to the



less frangible end, multiple observations before 1) and it was the same first from Swan on carefully examined in 1856 2); however, it did not make any wavelength determinations more characteristic

Carbon bonds, but determined the smallest for the first line of each group of the spectrum Deviation at the observation theodolite.

Dr. In 1880 Hasselberg reduced Swan's statements to Angstrom's

Values of the wavelength of the sun lines before 3) and made own observations about the Swan spectrum (in the visible part).

Hasse 1 b erg drove a constant stream of air through a layer of benzene about  $2\frac{1}{2}$  cm high in a Wollaston bottle; this gives a gas that is calm, with a beautiful blue cone and burns without danger.

Hasse 1 b erg observed that the spectrum burns brighter if you put oxygen into the side The flame blows and the carbon band in the red-yellow was shown, which without it Arrangement does not emerge; however, the dispersion of the spectral apparatus was not large enough to to resolve the partial bands in all lines (a. a. 0.).

The observations of various spectroscopists show that certain groups of lines of the Swan spectrum even when using incandescent means other than the Bunsen burner or Hydrocarbon-oxygen blower occur, for example using the induction spark, as well as in the electric flame arc (carbon electrodes).

1) Edinb. Transact., Vol. XXI.

2) The first mention is found in Wollaston: "Method of examining refractive power", Philosophical Transactions, 1802, who in his investigations into the solar spectrum draws attention to the difference that exists between this Spectrum and that of the lower blue mantle of a candle flame.

3) Hasse 1 b erg: «About the spectra of comets and their relationship to those of certain hydrocarbons», Mem. Acad. St. Petersburg, VII, Ser. I, XXVIII, No. 2, 1880,

J. M. Eder.

The four characteristic groups of the Swan band spectrum have already been observed by Pickering and Hittorf in the spectrum between electrical induction sparks when using Carbon electrodes in an atmosphere of hydrogen.

Angstrom and Thalen examined the spectrum of the discharge of the electric spark between carbon electrodes in nitrogen, hydrogen and oxygen. The real spark gives that Line spectrum of carbon, which differs from the Swan band spectrum of C. is; but the aureole or envelope of light surrounding it gives the Swan band spectrum or the band spectrum of cyan or carbon oxide 1).

The description of the characteristic bands of the Swan spectrum in the visible part on the part of the various observers is inconsistent as to how Live ing and De was (Proceed. Royal. Soc., XXX, 1880, pag. 152); the ultraviolet part became generally not precisely measured and very little is known.

In the visible spectrum, Lecocq mentions de Boisbaudran 2) in addition to the main bands ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  according to my designation) two more foggy bands in the indigo ( $\delta$ ). = 4368 and at  $\gamma$ ). = 4309).

Watts (Philosoph. Magaz., 1869 and 1871) gives the same lines, but broken up into a series of fine lines 3).

P l ü c k e r and Hitt o r f noticed the absence of two strong ones in the flame of ethylene characteristic blue and purple groups of lines of the cyan flame and the presence of one Series of dark lines on a purple background between the two cyano groups.

Morro n gives a similar description (Anna!. Chemie et Phys., March 1865).  
None of them noticed the presence of the above mentioned two foggy groups.

D i b b i t s (Pogg. Anna!. 1864) burned cyan in oxygen and noticed orange and red bands, shaded towards the breakable end, i.e. opposite to the first four bands of the S w a n's Spectrums; he also describes the cyan band in blue and violet.

J. Wesen d o n c k 4) in particular carefully compared the Swan spectrum and the carbon oxide spectrum,  
However, without fear of r ö m and Th a 1 e n new wavelengths of the carbon bands give; For the sake of clarity, however, the essence are also Donck's wavelengths included below.

S a 1 e t studied the spectrum, which with the help of the induction spark in luminous gas or cyan arises 5), but the wavelengths are only given in three places; but from this comes the identity of the first four carbon bands of the Swan spectrum with the bands investigated by him emerge.

Watts compared the Swan spectrum in 1869 (Philosoph. Magaz., 4th Ser., Vol. XXXVIII, pag. 249) (Burning of ethylene  $C_2H_4$  with oxygen) with other C-spectra and gave a figure to this Phenomena which is reproduced photozincographically in Fig. 1 (see pag. 3).

Fig. 1 a shows according to Watts the spectrum of the ethylene oxygen flame. In the flame of the He could not perceive the red group (a Watts) with an ordinary bunsen burner. The same spectrum

1

he observes the breakdown of the electric spark at ordinary temperature and normal

- 1) The lines of the associated spectrum of bands of carbon according to Angström and Thalen can be found at Kayser ("Spectralanalyse", 1883, pag. 247) as well as printed in Hasse 1b er g.
- 2) Lecocq: "Specters lumineux", Paris 1874, vol. I, p. 41.
- 3) cf. Kayser ("Spectralanalysis", 1883) and M. Watts ("Index of Spectra", 1889).
- 4) Wesen donck: "Investigations into the spectra of coal compounds", inaugural dissertation, Berlin 1881.  
(Very clear compilation of the relevant observations.) Excerpt in Anna l. d. Chemistry and Physics, 1883, Vol. XVII, p. 435.
- 5) Anna l. d. Chemie, 1873 (4th), Vol. XXVIII, pag. 60. Also Kayser, "Spectralanalyse", 1883, pag. 247.

The visible and the ultraviolet spectrum.

Air pressure, whereas ethylene and so on under reduced pressure another (later studied several times)  
Give spectrum.

Cyan, burned in oxygen, gives another red band, which is of a different character (in opposite direction shaded) than the previous bands have; those of Watts appear groups designated as y, ö and e (see Fig. 1). If, on the other hand, cyan burns in air, kick it more numerous bands (instead of the bands y Watts) on which Watts the compound cyan itself attributed.

Instead of the violet group found in the Swan spectrum (f after Watts, ~after mine Designation) Watts observed two brilliant groups of lines (~ according to Watts, from A = 460 to 450) and the purple band A = 422 to 416; Fig. 1 e shows the spectrum of the flame of cyan in air.

Fig. 1.

Representation of different carbon spectra according to Watts und Pücker.

Also in the spectrum of the induction spark striking through cyano gas at ordinary pressure

(see Fig. 1d) the W a t t'sche band f 1) is missing; the rest of the bands are partly those of Swan'schen

Spectrums, partly equal to that of the cyan flame.

Burning carbon oxide gives a continuous spectrum, but when the Induction spark through this gas at ordinary air pressure Watts obtained a coal spectrum, which soon became part of the Swan spectrum (inclusive was similar to Watts' group f),

soon the three groups e, ~'f) • (Fig. 1 [Watts]) also occurring in cyan (see Watts' Figure). The Spectrum I c was supplied by a Geyser tube with naphthalene.

Fig. II a, b gives the scheme of the

from Pücker he observed spectrums of carbon oxide in Geissler's tubes (induction sparks)

and the cyan flame, Fig. II b and c Watts' observations of carbon monoxide and ethylene in the Geissler's tubes at reduced pressure and penetrating induction sparks 2).

Later (Philosoph. Magaz., 4th Ser., Vol. XLVIII, pag. 370) Watts rectified the values for the Wavelengths of the bands designated by him with y, ö, e, which in my table 11 e n with consideration of these corrections are included.

1) According to H. W. Vogel, this band also occurs in the cyan flame, but weaker than in burning ones  
Hydrocarbons.

2) For the best understanding of Watt's scheme and comparison with my photographs of the spectrum of burning hydrocarbons I add that of Watts in 1871 (Philosoph. Magaz., 4th Ser., Vol. XLI, pag. 12)

communicated wavelengths along with the letter designations given in his scheme:

I \*

J. M. Eder.  
4th

Also the diagram given by P. Smith, which shows the spectrum of the blue flame of Coal gas and benzene vapor (burning with air) are because of the comparison with my results shown in Fig. 2.

Thollon (Compt. Rend., 1881, Vol. XCIII, pag. 260) observed a number of coal lines in the electric flame arc; With the same light source, Kayser and Runge<sup>1)</sup> determined the highest

Fig. 2.

Piazzi-Smith's representation of the Swan spectrum.

carefully examined the grating spectrum of the charcoal flame arc and obtained very reliable wavelength measurements  
numerous carbon and cyan lines after photographic spectrum images.

Although these investigations do not concern the same subject as those I have undertaken and the emission spectra of the burning hydrocarbons described here, so is their inclusion in the comparative overview of value because a number of C-lines both spectra is collaborative and reviewing these results gives an indication of what I have achieved Accuracy and about the characteristic peculiarities of those first measured by me Apply violet and ultraviolet spectrum bands to the Bunsen flame.

Own studies on the emission spectrum of the Bunsen flame and various hydrocarbons burned with oxygen by means of Quartz spectrograph.

In my investigations into the emission spectrum of burning hydrocarbons, I used them me of photography. The photographic observation of the spectra is not only the only reliable one

Method for studying the ultraviolet part of spectral phenomena, but it also gives in the indigo blue and violet parts of the spectrum far more reliable results than direct observation with the eye, which soon tires and for weaker light phenomena in the violet Spectral districts is extremely insensitive.

In the case of the spectrum photographs, however, I also took into account the less frangible ones

Rays. However, the four less breakable red, yellow, green, and blue bands are

Band rJ. Volume y Volume 1l Volume E Volume ~ Volume f Volume -0,

6190	5622	5170	4734	4600	4313	4261	4220
6110	5582	5139	4710	4574	4290	4256	4210
6050	5534	5100	4689	4550	4285	4249	4190

wavelength

5990	5495	5082	4675	4534	4279	4243	4174
------	------	------	------	------	------	------	------

5955	5463	4670	4514	4274	4239	4166
5440	4505	4268	4232	4160		
5425	4502	4158				

') <About the Spectra of the Elements •. Treatise d. prussia. Akad. D.Wissensch., Berlin 1889.

The visible and the ultraviolet spectrum.

Swan's spectrum in the visible (shining) part already several times and with great accuracy measured and only the violet and ultraviolet groups are not exactly known. It seemed to me

but of value, on my spectrographs, the entire picture of the spectrum in question from the Roth sharply defined down to the extreme ultraviolet, as such a spectrographic reproduction of the spectrum has not yet been reached at all and it is for the characteristic of the same of It is worth having such an overall picture in front of you. On the other hand, it seemed of interest to me that of m · ir determined wavelengths to be compared with the measurements already available, instead of to continue my measurements in the ultraviolet, those already determined by other observers Draw numbers in the table.

What especially the ultraviolet bands of the weakly shining blue Bunsen gas flame concerning, they were first found by me in 1886 by means of spectral photography, using a Steinheil glass spectrograph with three glass prisms. At that time succeeded after ½ to 2 days of exposure the resolution of the violet band e and the group ~ into numerous, well-defined lines and I discovered the ultraviolet group " / 1 of the Bunsen flame.

In the meeting reports of the Imperial Academy of Sciences in Vienna, 2nd Abth., XCIV. Vol.,

In 1886 (July issue) I communicated this observation and also published the reproduction of this spectrum photograph, which both on the well-known magnesium spectrum, as well as on the solar spectrum had been related. I didn't take the wavelength measurements back then because I was doing the experiments wanted to repeat with quartz apparatus in order to gain insight into the course of the spectrum in the ultraviolet to get.

Two years later, H. W. Vogel and E. Vogel jun. also the spectrum of the Bunsen flame with a glass spectrograph 1), but without penetrating further against ultraviolet, when I succeeded at the time.

In order to prevent any error, I notice that these ultraviolet bands of mine are already as mentioned above, had been found 2 years earlier and published in collotype.

Although neither Prof. H. W. Vogel 1 nor I myself used wavelength measurements at that time

Glass bodies had made spectral photographs of the Bunsen flame, so it turns out nevertheless, from the published collotype, the identity of the two in question photographed by us Spectra.

Precise measurements of the wavelengths of the bundles of rays in the emission spectrum of the Bunsen flame

in the violet and ultraviolet parts (volume 5, ~ 1/1, {1}) are not yet available.

I therefore subjected all the coal bands of the Swan spectrum, but especially those I discovered ultraviolet bands of the Bunsen flame 1/1 and {1}, an exact measurement of which Results are later compiled in tabular form. Description

of the quartz spectrograph used.

In my experiments I endeavored to cover the entire spectrum, from the red part to the extreme ultraviolet, to be photographed on a plate using quartz bodies; just this way a typical picture of the peculiarities of a spectrum can be produced, which is just as important for absorption than emission spectra is.

As Mr. V. Schumann pointed out 2), the difficulty lies in the very extensive Spectral district from  $\lambda$  7600 to 1988 (aluminum no. 30), which is the subject here

- 1) Meeting area d. prussia. Akad. D. Wissensch., Berlin 1888, Vol. XXI (April).
- 2) Eder: "Yearbook for Photography and Reproduction Technology", 1890, p.159.

J. M. Eder.

photograph, in that the curvature of the diacaustic of the lenses is a hindrance. According to her, appears such a picture is only partially sharp. From the point where the diacaustic and plate meet - which usually happens in the middle of the spectrum - the image sharpness decreases towards both sides.

So far, this problem has been circumvented by not opening the whole spectrum once, but takes up both halves one after the other, and each time the misalignment of the light-sensitive Plate adjusts to the focal surface of the lens. Such separate recordings cannot be used when it comes to getting a typical picture of the whole spectrum at the same time, like it seemed to me of particular value for my experiments.

About the use of the quartz and white achromatic lenses recommended by Mr. Cornu I had to refrain from using flux 1) because colorless flux with perfect transparency is not available.

In his recordings, Hartley placed the ultraviolet on the cadmium line No. 17 ( $\lambda = 2743$ ) into the minimum of distraction. All other rays then pass through, regardless of whether they are more breakable or belong to the other half of the spectrum, the prism is not symmetrical and as is known,

the more the line image loses its sharpness the further it moves away from the minimum of the deflection.

V. Schumann in Leipzig, to whom we owe the most precise studies with the quartz spectrograph

and who helped me with advice and deeds in the preparation of my spectrograph,

gave me his observations on this kind of attitude (after Hartley); he found the two halves of the spectrum differ in clarity • and that the less breakable the better is defined by both. This difference becomes even more noticeable when one looks at the ultraviolet entirely

disregards and only operates with the visible spectrum.

If you then bring, for example, the yellow sodium line of a table salt flame into the position of smallest deflection and rotates the prism, so the so-called line will lose little of its sharpness, as long as the angle of incidence, which the rays coming from the gap with the first refracting surface

form of the prism grows; on the other hand, their purity becomes rapid with unusual broadening go back as soon as the said angle decreases. V. Schumann made use of this fact to redesign the previously curved diacaustics of the quartz lenses into as flat a surface as possible.

For this purpose, the prism is not used, as before, for cadmium line No. 17, but for the most breakable line of zinc # 29 into the minimum of deflection.

The length also depends on the inclination of the first prism surface to the axis of the collimator of the spectrum. By suitably covering the prism, the spectrum length can be changed in such a way that

that the picture, especially in the end districts, visibly gains in purity. -Not without

The lengths of the camera and the collimator influence the end result. Tubes of the same length don't give the best results. With a moderate shortening of the collimator and a corresponding lengthening

The camera achieves more uniform sharpness than ever before over the entire spectrum.

The determination of the most appropriate mutual position of the collimator, prism and plate is a time consuming job. It goes without saying that only the results of the photographic Observation are crucial.

With my quartz spectrograph made according to these principles of humanity I spectrum images of). = 7600 (Roth) to). = 1988 (aluminum no. 30) with completely sharp Definition which allowed the measurement with the greatest possible accuracy.

The "quartz lenses" were cut from the purest mountain crystal (perpendicular to the optical axis);



they casually had a focal length of 75 cm for the yellow sodium line. Both lenses were plano-convex and symmetrical. The radius of curvature was 392 mm and the diameter 38½ mm.

1) Co r n u: «Representation of the photographic spectrum from violet to line No. 32 of the aluminum on the same Plate »(Eder:« Yearbook for Photography and Reproduction Technology », 1889,pag. 267).

The visible and the ultraviolet spectrum.

One of these lenses served as a collimator lens, the other as a photographic objective. The quartz prism

was (according to Co r n u) two-holy; each part was a 30 ° prism, one on the right and the other was turning to the left. The two half-prisms were cut perpendicular to the optical axis, as in FIG Fig. 3a is expressed. Both halves were put together<sup>1</sup>) and then gave a combined 60 ° refractive angle prism.

As a result of the use of non-achromatized quartz lenses, the sensitive plate had to be strongly be tilted against the axis of the camera lens; is the union distance of the ultraviolet rays namely, under the above conditions, considerably shorter than those of the red and yellow. vVie already

mentioned, the location of the sensitive plate must match the location of the focal surface of the quartz lenses can be adjusted. In the case of FIG. 3.

The apparatus I used is the inclination of the plate about 25 °, which is the angle between the plate and the axis of the lens. This misalignment of the plate is the spectrum image is extended 2½ times. /

Optical axis

The dispersion thus apparently grows (as already Sc human n 2) draws attention), but of course also the Verfl

7,

ratio of the width of the spectrum lines. It is this increase in length as clockwise rotating quartz · The spectrum, in view of the weak dispersion of the left-rotating quartz Quartz, a notable advantage and since it is only from the

Chromasia of the camera lens results, so the simple chromatic quartz lens is an achromatic one In this case, quartz flux path objective is definitely preferable. The plate format for my Spectrum photographs

is 30 cm long and 8 cm wide. By using the Locky e r's gap with

If the position of the photographic plate has not been changed, five spectrum recordings can be latched one above the other

do. The cassette can be shifted 4 to 5 times, so that on a plate 4 to Take 5 pictures with the full slit width or 20 to 25 pictures with a partially open slit

to let. Of course, the dispersion of the quartz spectrograph in the optically bright (visible) Spectrum low. The extension of the spectrum from the yellow Na line (D) to the end of the violet

(Line H of the solar spectrum) is  $3\frac{1}{2}$  cm, whereas the length of the ultraviolet spectrum is H. ( $\lambda = 3968$ ) to the cadmium line ( $\lambda = 2147$ ) = 20 cm. The study.

The room in which the observations were made was utterly darkened, and it became ensure that the temperature is as uniform as possible. In fact, even the four days worked continued exposure does not result in the detectable doubling of any line.

Still I turned

the caution that I use the metal comparison spectrum after a longer exposure time

the first half of the total exposure time while the Bunsen flame is burning and

photographed through it onto the silver bromide plate. This was intended to result in the

Comparison spectrum with reference to the mean level of the Spectrograph to attach, in the case of

Bunsen burners burning continuously in front of the gap should have brought about a slight change.

With this arrangement, the heating of the splitting slide was approximately

$28^{\circ}\text{C}$ ., while the air temperature in the

room was an average of  $17^{\circ}\text{C}$ .

1) Without any binding agent. Canada Balsam is quite unsuitable for the photography of the ultraviolet; would be against it

thick glycerine can be used, which absorbs ultraviolet rays very little.

2) Eder: "Yearbook for Photography and Reproduction Technology", 1889, p.233.

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Treatment of photographic plates.

The photographic plates used were high speed silver bromide gelatin plates from a sensitivity = 23° of the Warnerke sensitometer.

In part, self-made iodobromide silver plates (using silver oxide ammonia according to Eder's Method produced 1), partly also plates from the emulsion plate factory of Dr.

Schleussner

in Frankfurt a. M. used. Of course, the emulsion must be applied to mirror glass.

The plate format was 8:30 cm. Pyrogallol soda or pyrogallol potash, which were used as the developer

Type of development for the sharpness of the spectral lines proved to be decidedly more advantageous than that in

Hydroquinone or eikonogen developer often used in photography recently.

For the self-prepared silver oxide ammonia plates I usually used one of the following

compound pyrogallol-soda developer:

A. 100 g neutral sodium sulfate (crystal)

500 cm<sup>3</sup> of water

6 drops of concentrated sulfuric acid

14 g pyrogallol.

B. 50 g of crystallized sodium carbonate

500 cm<sup>3</sup> of water.

C. 1 g of potassium bromide

10 cm<sup>3</sup> of water.

Before use, mix 1 volume A with 1 volume B and 1 volume water; develop the Plates in this mixture are not completely veiled, so add developer 4 bis to about 50 cm<sup>3</sup>

Add 6 drops of potassium bromide solution.

Sch 1 e u s s ner plates and other less powerful, highly sensitive gelatin emulsion plates

I developed a potash solution

D. 50 grams of calcined potassium carbonate and

500 cm<sup>3</sup> of water

produced and used in the above procedure in place of the sodium carbonate solution; it is enough half the amount of the potash solution, namely

20 cm<sup>3</sup> A (pyrogallol solution)

10 cm<sup>3</sup> D (potassium carbonate solution)

20 cm<sup>3</sup> of water

and 4 to 6 drops of potassium bromide solution.

The fixer is acidified sodium hyposulfite solution, namely

250 g sodium hyposulfite (fixing soda)

1 liter of water

50 cm<sup>3</sup> concentrated sodium bisulfite solution 2).

In this acidic fixer, the negatives become very clear and lose any trace of yellow coloring. the gelatin layer, which the plates developed with pyrogallol often show.

If the yellow and green rays are to be taken into account when photographing the spectra,

so one makes use of orthochromatic plates, which I always use from ordinary Bromsi!

Bergelatin plates by staining with erythrosine or erythrosine silver parstelle.

1) S. Eder: "Photography with silver bromide gelatin plates", 1890 (Knapp, Halle a. D. Saale).

2) Namely concentrated sodium bisulfite solution which is supersaturated with sulfur dioxide. Such solutions come

on sale at cheap prices and are currently widely used in practical photography (see Eder: «Photography

with bromosilver gelatin », 3rd edition, 1890, pag. 309). The visible and

the ultraviolet spectrum.

A solution is made of 1 part of erythrosine 1) and 1000 parts of water and, on the other hand, one

Solution of 1 part of silver nitrate in 80 cm<sup>3</sup> of water. Be before use

25 cm<sup>3</sup> erythrosine solution

1 cm<sup>3</sup> silver nitrate solution

½ cm<sup>3</sup> = 8 drops of ammonia (density = 0.91)

and 75 cm<sup>3</sup> of water

mixed, well filtered and put through an ordinary emulsion plate in the darkroom

Bathed for 1 minute 2). The panels are dried and held freely in the air in total darkness then for 2 to 3 days. The

measuring device.

To measure the position of the spectral lines on the photographic negatives, very

Accurate measuring devices are used, with which one can quickly get larger stretches of the negative

and can measure safely. My measuring device was based on the model of the tried and tested V. Schumann's

Instrument 3) by Mr. E. v. Gothard designed and manufactured in Hereny.

The same thing consists of the following: A millimeter rod (from Wanschaff, Berlin) serves as a scale

which the reading takes place by means of a reading microscope; in permanent connection with the microscope

a second microscope moves, which is used to adjust the spectral lines. The micrometer thread

Fig. 4. Fig. 5.

in the ocular screw micrometer, only one millimeter is used; larger distances are read on the millimeter rod. 4 and 5 show the rear and side views of the instrument.

A in Figures 4 and 5 is a solid iron table, which with the iron prism (PP) and the iron Table (oo) is firmly connected. The slide (C) is placed on the prism (PP), which should be through

own weight rests on it and the two observation microscopes (a and b) with the massive,

permanently connected bracket (m) carries. The carriage has a rough movement by means of a rack and

Screw; A micrometer screw is attached for fine movement, which is also open a separate small slide rests, the jaws of which enclose the prism and on this -an

Any point - can be clamped with a clamping screw. The upper part of this before

- 1) The types of erythrosine on the market are very different; I always use Erythrosin from Dr. Schuchardt in Görlitz.
- 2) The cup must always be swiveled to avoid stains.
- 3) S. Konko 1 y: "Instructions for sky photography", 1887, p. 191.

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direction is borne by the micrometer screw. This screw connects the reading microscope to the Slide (c) on which they are attached, pushed from right to left; this movement is very safe, but is only used for setting free on short stretches. Fig. 6 shows the table on which the Spectral negatives can be clamped or fixed with adhesive wax. On the table (o in Fig. 4 and 5) is a

flat frame (g in Fig. 6) on which a movable frame (f) is located. This turns around the pin (o) and can be moved with the screw (l) in such a way that the spectral lines of the plate to stand perpendicular to the movement of the slide carrying the reading microscope (c in Fig. 4 and 5) come. The negatives are

Fig. 6.

men (f) clamped so they can feel during

of reading do not move. The millimeter rod (e) is by means of two columns with connected to the frame (g). The spectral negatives are measured from below illuminated by means of a mirror (s); sometimes take the spectral lines in the microscope better true if instead of the mirror one white porcelain plate used as a reflector becomes. The one reading microscope (a and b) is on the micrometer rod, the other on

set the negative; the former is with an ocular micrometer, the latter only with a St. Andrew's cross

Mistake. The magnification is 20 times.

The micrometer screw in the microscope (a) has 10 turns per millimeter and the drum is in 100 parts divided. The setup of the micrometer device is shown in FIGS. 7, 8 and 9 (Konkoly, loc. Cit.).

a is the microscope tube on which the square box (CC) is placed; in this moves the frame (c in FIG. 7) on which the two parallel threads visible in FIG. 9 are stretched are; In this frame is also the nut thread of the micrometer screw (S), which is on its outer end carries the drum (T) and the button (K in Fig. 7). The dead corridor of the micrometer

Fig. 7. Fig. 8. Fig. 9.

The screw is suspended by two spiral springs ( $f$  and  $f'$ ). The plate (b), spring ( $f''$ ) and screw (a) serve to collect the zero point of the count (Fig. 8).

The measurement of the spectral lines, in which mine, as well as in part of those described here Attempts to get Mr. J. Hof and Mr. Ritter v. Reisinger assisted, happened directly on the original negatives, which were cemented onto the measuring device by means of adhesive wax in such a way that a shift was not possible without the use of force. Setting the crosshairs of the measuring device to the Spectral lines always occurred in the middle of sharp lines. For blurred lines, especially in those which (like the lines of the band spectrum of carbon) against the one Side are in focus, gradually weakening towards the other, and become weaker with longer exposure wider, it is more difficult to adjust; namely, neither the position of the sharp edge is constant nor the middle of the wide strip.

The visible and the ultraviolet spectrum.

The reason is that the sharp edge is slightly smaller when the exposure is extended Amount shifts as a result of the broadening, on the other hand the gradually blurred side of a such a line widened disproportionately more with prolonged exposure. For this reason the adjustment to the sharp edge as well as to the center is uncertain. On the other hand, one obtains constant, comparable numbers, if one reads such one-sided blurred lines as follows undertakes: one brings the light source in front of the gap in such a way that it does not completely fill the gap covers the same way, but in the middle of the gap there is a stronger light effect than at the ends of the same. You can achieve this, for example, if you put a stream of oxygen in luminous gas introduces, so that a small, intense, blue flame cone is formed, which is only half of the Gap covered. This gives mon spectrographs on which the lines in the middle are strong, but gradually become narrower at the ends and finally lose themselves completely. On these narrow ones At the ends, however, in a direction parallel to the center of the spectrum band, the adjustment is made with certainty and the reading represents the maximum of the effect (brightness) of the relevant Spectral lines. Of course, these readings differ from those for the sharp edge is set; for example in the case of the carbon bands  $\sim \lambda$ ,  $\alpha$  etc. are those from the former Readings calculated wavelengths slightly smaller than those determined by the latter method Numbers.

For the reasons mentioned, however, the reading from the middle of the seems to me to be gradually weaker becoming and finally thin line, at that point where it has already narrowed significantly, but it is just now clearly visible to be the most accurate and correct; in this phase the Measurement of the entire lines of the Swan spectrum.

The Preparation of the Hydrocarbon Flame and the Comparative Spectrum Photographs of the former with the metal spectra.

To observe the spectrum, the blue lower cone of flame became one B using a gas burner. It had a tube diameter of 2 cm; the upper part the tube is made of thick platinum sheet so that the flame is not contaminated. This platinum tube Easily taken down so that it can be carefully boiled before and after each attempt could be cleaned with water or nitric acid. Air access to the burner was so plentiful that there is no trace of a glowing fringe on the non-glowing Bunsen flame noticed.

One series of experiments was carried out with the use of a quartz condenser - another without Condensor - so that the flame is brought about 8 cm in front of the platinum gap of the collimator tube has been. In the first-mentioned arrangement (see um an n'scher condenser with crossed quartz cylinder lenses) the spectrum image was weaker. There the blue flame cone of the B us nian gas burner copiously covered the entire height of the slit of the spectrograph, so on direct installation of the flame in front of the gap on the photographic plate obtained spectral photographs, which gave the lines corresponding to the full length of the gap.

Similarly, the Linnemannian oxygen blower was set up in front of the gap and with hydrogen, which with luminous gas, oxygen or hydrogen, benzene vapor or petroleum ether was saturated 1), fed.

1) This was done by introducing the gas into three Wo u lff bottles, one behind the other, half of which were filled with benzene, etc., so that the hydrogen had to pass through the hydrocarbon layer several times. The hydrogen was developed from the purest zinc and sulfuric acid and more concentrated by washing with silver sulfate solution and caustic potash Sulfuric acid purified.

2 \*

J. M. Eder.  
The comparison spectrum.

For the production and simultaneous photographing of a comparison spectrum, one was used

The spark spectrum of an alloy of cadmium, zinc and lead (in equal parts) goes to great fame

generated. The Ruhmkorff'sche inductorium made it possible to achieve a sparkwidth of 25 cm.

The electric current was generated by means of six large elements (platinum-coated lead with Chromic acid, amalgamated zinc in a thin junction with dilute sulfuric acid); the

The battery was freshly filled with 17 amps and 12 volts. The spark was switched on

Reinforced by three large Leydener bottles. The distance between the metal electrodes was approximately 2 mm.

The spark generator was set up at a distance of 40 to 50 cm from the slit of the spectral apparatus,

so that the gutta-percha parts of it do not even when the gas flame is kept burning

Could suffer damage. The metal spark flashed over in the horizontal direction and further became the same

brought in front of the middle of the gap. In this way I achieved that a sharply defined spectrum of the alloy

emerged in the middle of the plate. The gap was (after Lockyer's Fig. 10.

Process) covered by five small sliders, which are successive could be opened or closed. The spark spectrum of the

I photographed cadmium, zinc and lead alloys with the open Middle bar

with an exposure time of 10 to 20 minutes; while

During this time, a perfectly strong, well-defined photograph is created of the metal lines, not just the main lines, but

also the weaker lines precisely determined by Hartley (1).

This makes a sufficiently uniform look over the image area extensive comparison spectrum obtained, which is so vigorous

is that it is caused by the Swan's spectrum, which is also photographed in it

Well is recognizable. To those belonging to Swan's spectrum Easily and reliably distinguish lines from those of metal alloys to be able to, I let us see the spectrum of the B

Take effect of the flame with the slit fully open. It spreads accordingly

F.

A.

on the spectral photographs that were finally obtained, the Swan'sche Spectrum with twice the length of the lines above and below the comparison spectrum.

This makes it much easier to measure the lines and significantly increases the accuracy. The

However, photographing several spectra on top of one another gives rise to ambiguities where the Plate is hit by bright lines of different spectra.

In this case the spectra must be photographed side by side without the photographic



The plate or the spectrograph may be changed; this is done by means of the before Gap located bolt.

The greatest care must be taken when photographing two spectra to be compared one on top of the other

to lay the correct axial incidence of light from the light sources to be observed. Setting the Metal sparks were made by inserting a small round aperture close to the collimator lens and then the light slit image with the one recommended by Schumann, in front of the middle of the

Prism located mirror 2) was observed. The regulation of the height of the induction spark happened to a eug. von Gotha r d'schen spark generator, the device of which can be seen in Fig. 10.

1) If the metal spark is not generated exactly opposite the middle slit opening, the spectral lines correspond not along the entire length of the middle gap length, but become shorter and sooner than longer, sooner than shorter lines.

"-) S. Konko 1 y:" Instructions for sky photography ", 1887, at W. Knapp in Halle a.

The visible and the ultraviolet spectrum.

It is similar to the apparatus designed and successfully used by V. Schumann adjustable tubular stand (A), the rod (B) moves up and down (by means of a rack and screw) downwards and can be clamped with the screw (a). The thick ebonite disc (E) has two Brass bearings (F, F'), which hold the two strong brass rods (bb); these bars are round at gg

Drilled out to accommodate the electrodes, which are clamped with the help of the screws (ff) become. The ends of the brass rods carry large ebonite disks with which one can distance the electrodes

can also change during the course of the inductorium. On the back of the ebonite disc (E) two brass rings (cc and dd) are attached, one of which is marked with F, Fig. 11.

the other is in conductive connection with F'. The binding posts are on the Ebonite stand (C) put on and with brass springs with the rings (cc and dd) in contact brought. . ~ ~

The disk (E) can be rotated as desired about its axis (D), always with the ~

the power remains on. The axis (D) is hollow and can inside

slightly a cylindrical rod made of steel, which, as FIG. 11 shows, extends into a point (S), back and forth

be pushed around. This cylindrical rod is used (as in Schumann's process) to adjust the exact location of the spark. The electrodes are always approached to the tip

(S) in the same way

to bring it constantly to a definite place; slight deviations in the position of the electrodes

that is, causing the metal spectrum to move back and forth on the photographic plate, what

must be avoided in experiments on the coincidence of lines. You can also see the consequences of the

uneven wear of the electrodes during a photograph, not just by

Switch the poles, but also make it harmless by turning the disc (E) by 180°. The reference

spectrum.

The Hartley-A and the Fraunhofer numbers 1) were chosen as reference lines, since they work well with the

from Liveing and De Wailly's given numbers (Philosoph. Transact., 1883, Vol. CLXXIV, Part. 1,

furthermore a philosopher. Transact., 1888 2) for the wavelengths). > 2370 Å (3). (NB. In

later examinations

Rohrbaugh's standards were chosen; see later.)

The measurements of the spectrum negative and the wavelengths calculated by interpolation of the spectra cited in this treatise I referred to the following lines of the same

Partly made alloy of cadmium, zinc and lead, on some characteristic lines,

as well as in individual cases on the magnesium spectrum also photographed (in the induction spark).

1) Hartley and Fraunhofer: "Measurements of the Wavelengths of Lines of high refrangibility in the Spectra of elementary

Substances" (Philosoph. Transact. Of the Royal Soc., 1884 [in excerpt: Watts: "Index of Spectra", Manchester 1889]).

2) In excerpt: Watts: "Index of Spectra", 1889.

a) cf. A. Grünwald, meeting area. d. kais. acad. d. Wissensch., 2nd Abth., Vol. XCIII, pag. 791, Vienna 1890.

Angstrom units 10<sup>-7</sup> m

and others happened. The precision

My measurements in the visible spectral region mostly extended to Eine Angström 'see

Unit; in the ultraviolet, where the dispersion is much greater, see, on the other hand, up to 1/10 Angström '

Unit.

That is to say, it corresponds to 159 parts of the measuring apparatus used by me, for example in the

Yellow between Pb = A = 5607 to Cd = A = 5378 One Angstrom unit; in the blue between Cd = 4799 to zinc = A = 4721 correspond to 230 parts of an Angstrom unit; in the ultraviolet between Zn = A = 3344 to Zn = A = 3302 653 parts correspond to an Angstrom unit and between Pb = A = 2613 to Zn = A = 2608 1346 parts correspond to an Angstrom unit.

Description of the emission spectrum of the burning hydrocarbons (Swan's spectrum) based on my investigations.

In the emission spectrum of hydrocarbons that burn with oxygen (blue flame cone) one can distinguish two main types of spectra:

1. The bands belonging to the carbon or hydrocarbon.
  2. The spectrum associated with the burning hydrogen (water vapor).
- 1) «On the spectrum of the elements». Treatise of the royal prussia. Akad. D. Wissensch., Berlin 1889.

The visible and the ultraviolet spectrum.

I. The burning cone of hydrogen or cone of the Swan's spectrum.

In the spectrum of the burning luminous gas or other burning hydrocarbons, which burn with sufficient amounts of air or oxygen to produce a faintly glowing blue color. Shows a cone of flame, eight luminous bands appear when observing in the quartz spectrograph, which consist of more or less numerous bright lines, which differ from a non-luminous one. Stand off reason; In individual parts of these bands, next to the light lines, there is a weakly glowing line. Continuous spectrum, which at the most intense parts of the band more or less appears clearly, fulfills part of the band and runs in the direction of the less bright one. Side of the band soon ends. This continuous luminous spectrum from which the stand out in lighter spectral lines, occurs especially in the visible part of the spectrum with the bands' { and ~, but is more or less noticeable in all bands observed. The ones known so far including the bands of the so-called Swan's which I found in the C-Spectrum divide into two distinct groups according to the structure of the lines of which they are composed.

1. The first group of C-bands of the Swan's spectrum, which against the less breakable end to have the strongest lines and a sharp, strong edge in the same direction show, while the following lines gradually weaken towards the more breakable end and follow one another at great intervals; this is where the hitherto known volumes 7-, ~" (, ~

and the band that I first measured exactly (.

2. Second group of lines of the Swan spectrum, in which the arrangement of the lines and the bands are shaded in the opposite direction; here with is the characteristic one Boundary line of the band is located towards the breakable end and connects to this in the direction

of the less frangible part of the spectrum a band consisting of numerous lines which the lines weaken in the same direction; at the same time the lines follow against that less breakable end to at ever greater intervals.

Here belong three bands in the outer violet and ultraviolet part of the spectrum and have not yet been described in the Swan spectrum of burning hydrocarbons.

These are the homologous bands e, some of which have been newly found by me, some of which have been measured first,

"f) and {} \_ It is characteristic of these groups that the one turned towards the more breakable end

the strong end line of the same is clearly isolated from the one towards the less breakable end shaded line group.

This is particularly noticeable in the case of the group 'f), which is typical; the construction of the

Group, ~ ·, which, however, is 5 to 10 times fainter than the former; in my opinion also belongs the ties to this group of groups. For all three bands show the peculiarity that in addition to the dense group of lines shaded towards the less breakable end

have a single line, which at a short distance, but still clearly isolates, to join the mentioned group of lines against ultraviolet (see Plate I, where the construction of this band can be seen most clearly in the reproduction at 'f)).

In the case of volume s, this analogue line structure is less clearly visible because the three lines 1. = 4380, 4372, 4364 1) store in the band e and probably not to the actual, against Roth belong to shaded line group e 2).

1) There are three lines that appear particularly strongly in the burning cyan. D. K a y s er and Runge lead them

as the three edges of the five C bands (in the electric flame arc between carbon electrodes).

2) In my tables and figures, the entire band from), = 4380 to 4325 is referred to as "Band E"

because it appears as a closed group when looking at the spectrum.

J. M. Ed er.

Individual description of the groups.

The red band r: t .. appears in the ordinary Bunsen flame as a faintly visible one Blurred band, which only clearly dissolves into lines when oxygen is blown in.

The clear, red group of lines appearing on the admission of oxygen shows in apparatuses of moderate value

Dispersion (1 to 2 glass prisms) five lines.

The group appears particularly good when the luminous gas is mixed with benzene or petroleum ether, etc.

is saturated before it is burned.

The green band  $\beta$  occurs much more clearly in the ordinary Bunsen flame, consists of five lines, of which the least breakable is the strongest and the lines towards the breakable end

weaken. The last line ( $\lambda = 5570$ ) is hardly visible in the ordinary Bunsen flame.

If the hydrocarbon burns with oxygen in the fan, the brightness of this band increases considerably

strong. In the photograph the five lines I measured are clearly visible; they appear bright on a faintly shining continuous base, which continuous spectrum still extends over the last clear line ( $\lambda = 5570$ ). This tape is only available on erythrosin, or eosin

similar - so-called «orthochromatic» plates can be photographed. On ordinary plates it does not appear (see Plate I, Spectrum 2 and 3).

The green band  $\gamma$  is particularly intense and appears in the spectroscope as the independent band

the Bunsen flame or the luminous gas oxygen blower. It consists of three very bright lines, from the least breakable line ( $\lambda = 5164$ ) is the brightest of the entire visible spectrum.

The tape is similarly shaded against the more breakable end and the lines are more similar

Way on a weakly luminous ground, as in the case of tape  $\beta$  (see Plate I, Spectrum 2 and 3). Also

this band can only be photographed on erythrosine plates, etc., as panel I, Figs. 1 and 2 shows, where the group is missing in the former (this photograph is on ordinary silver-bromide gelatine plates

manufactured), but is clearly visible in Spectrum 2 and 3 because an erythrosine plate was used,

which is insensitive to yellow and green.

The blue band  $\delta$  is less intense in the Bunsen flame than the previous one (band 1), but

slightly brighter than band  $\beta$ . It consists of five lines. Becomes oxygen in the hydrocarbon

blown, the lines become lighter, but at the same time the continuous weak spectrum wins, on which these lines appear, essentially in brightness. Let this group and the following

can also be photographed well on ordinary silver bromide gelatine plates.

The violet band is faintly visible and appears as the spectrum of the Bunsen flame

often only as a blurred strip, the center of which, according to Leacock, has the wavelength = 4368. in the

Coal gas oxygen blower, or even better with very lively combustion of benzene vapor. Oxygen, the band is also visible to the eye and is broken down into a system of lines.

In the Bunsen flame I first dissolved this tape into lines and photographed it.

The measurement of the lines succeeds both on these spectrophotographs of the Bunsen flame, as well as also particularly good at photographing benzene flames with an oxygen blower; in the former case a weaker, in the latter a stronger, continuous spectrum emerges, which is connected to Long exposed or denser negatives make the lines barely noticeable.

The characteristic appearance of this band can be seen on Spectrum 1, 2 and 3 (Plate I); the fine lines were partly lost in reproduction.

Immediately afterwards follows a single strong line, which is characteristic and appears more intense than any line of bands in the photograph. The line ( $\lambda = 4325$ ) corresponds to me, as well as the numerous lines of the whole band in the Bunsen flame and the flame of other burning hydrocarbons, found and measured.

The visible and the ultraviolet spectrum.

The violet band  $\sim$  is extremely characteristic. This is the most photographically effective band of the total band spectrum of the carbon and occurs even with very short exposure at  $\lambda = 431$  a clear one-light effect on.

The lines are numerous and regularly distributed, and are shaded in front of the less breakable ones towards the more breakable end, becoming weaker and weaker.

According to the investigations by spectroscopists available to me, this band does not occur in the electric arc of flame before (Thollon, Kayser, Runge and others), just as little in the spectrum of the with carbon dioxide-filled Geissler tubes (induction spark).

A line-rich cyan band begins (according to Kayser and Runge et al.) at  $\lambda = 4216$ , i.e. at a place where the lines of my carbon ribbon (already begin to end; this cyan ribbon is therefore with the band occurring in burning hydrocarbons  $\sim$  'which at  $\lambda = 4310$  (with short exposure) or with  $\lambda = 4315$  (with long exposure) occurs most intensively, not identical 1), but the latter is a highly characteristic band of the so-called Swan spectrum.

Strangely enough, Swan himself did not notice this band; this should be due to it find that strongly refractive glass prisms already have the violet in the districts  $\lambda = 431$  to  $420$  and further absorb very strongly, and therefore have such a spectrum for direct observation with the eye is too faint.

Prof. H. W. Vogel explains after his photographs of the Bunsen flame and the cyan flame, that the limit of the band from  $\lambda = 431$  with  $\lambda = 420$  (by me with  $\lambda = 420$ ) marked absolutely with the broad sun lines (G) and that the dark background of the Fraunhofer G band the solar spectrum is therefore to be assigned to carbon<sup>2)</sup>; Prof. H. W. Vogel had the wavelengths of the carbon lines in question were not measured, but merely from those photographed one above the other Spectrum images drawn his conclusions.

The measurements I made of the spectrographs of the Bunsen flames or those with oxygen burning hydrocarbons resulted in  $\lambda = 4315$  as the most intense limit of the carbon band longer exposure (consequence of the broadening due to the strong light effect), on the other hand  $4310$  to  $4312$  at short exposure; on the other hand, the wavelength of the sun line is  $\lambda = 4307$ .

This difference is too great to be able to deduce coincidence from it.

The ultraviolet group n of the Bunsen flame is much fainter than the group  $\lambda = 431$ ; the brightness the former is only  $1/10$ , to  $1/100$  of the latter. The band  $\lambda = 431$  is immediately noticeable because it is in opposite side is shaded than the characteristic bands in the visible spectrum, namely the red 'X', the yellow  $\lambda = 589$ , the green  $\lambda = 546$ , the blue  $\lambda = 486$  and the violet ( $\lambda = 431$  group).

Furthermore, it is very characteristic of this group that to those, regularly distributed from many, towards the red end of the spectrum, a strong, isolated band of lines shaded line connects; the strongest line of the shaded line band is at  $\lambda = 3889.8$ , then some follow very faint lines and then at  $\lambda = 3873$  a strong, intense, single line, which the whole group  $\lambda = 431$  too limited against ultraviolet. The peculiar structure of this group emerges clearly  
Plate I, Spectrum C-Band  $\lambda = 431$ .

The group  $\lambda = 431$  appears even in the weakest flame of the Bunsen burner, a lot more clearly, however, in burning benzene or petroleum ether, which with oxygen becomes intense

1) According to Salet (Annales de Chimie et Phys., 1873, Vol. IV, pag. 60) the electric spark in luminous gas or cyan gives the

Bands  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$  analogous to the Swan spectrum. The combustion of hydrocarbon and cyano gas, the latter in pure oxygen, gives the same band ( $\alpha$  619,  $\beta$  563,  $\gamma$  516,  $\delta$  464), but the purple part is different; instead of a tape at 427 (after Kayser 422) there is a lively band). = 431 to the fore, which from a breakable part with fine cannellations followed up). = 418 extends (cf. also the figure given by Vattson).

2) meeting area d. prussia. Akad. D. Wissensch., Vol. XXI (1888).

J. M. Eder.

Combustion is brought about with a blue flame cone. This is characteristic of burning Hydrocarbons.

The ultraviolet band  $\delta$  occurs only with a very long exposure and is used in one for measuring. Obtain the necessary clarity if you work in the Linnemann'schen blower for 4 to 5 hours. Coal gas or hydrogen and benzene vapor or petroleum ether burns with oxygen.

The structure of this group is completely analogous to  $\gamma$ . A number of regularly arranged lines, which become too weaker towards the red end give one that is too shaded in this direction. Band, whose strongest line is at  $\gamma$ . = 363 x 45; this is followed by the singular, likewise characteristic Line). = 3627, which forms the boundary of the group towards the more breakable end.

After these experiments I also studied the spectrum of the burning Kohlen

oxydes.

However, live in  $\gamma$  and  $\delta$  had already indicated that burning carbon dioxide was a there is a continuous spectrum. I photographed very sensitive ones by exposing them for several hours

Plates in the quartz spectrograph the spectrum of the carbon oxide flame and likewise only received

a continuous spectrum, which extends over the entire spectrum, but especially between  $\gamma$ . = 430 to about  $\delta$ . = 330 made noticeable.

Also 5 hours exposure to a mixed carbon-oxide-hydrogen flame (burning in the air, as well as in the oxygen blower) there was no line spectrum 1).

The bands of the spectrum of the Bunsen flame or hydrocarbon-oxygen-Flame does not belong to the burning carbon monoxide.

The brightness of the continuous carbon oxide flame spectrum is opposite to that of Swan Band spectrum so faint that one can say the blue-green flame cone

The Bunsen flame owes its weak luminosity mainly to the band spectrum of the Carbon or hydrocarbon, but not the burning carbon monoxide. The upper one, almost



The Swan band spectrum shows the colorless and extremely weakly luminous part of the Bunsen flame in a much weaker (less bright) degree than the blue flame cone; nevertheless it can be with the help of spectrum photography, the appearance of the characteristic carbon bands also in this part prove. But it is mainly the almost colorless upper part of the flame that sends the water vapor spectrum off.

The complete separation of the hydrocarbon flame into a blue flame cone, which is the Swan band spectrum and an almost colorless upper flame cone, which is just that Water vapor spectrum is achieved by blowing oxygen into a luminous gas, benzene, Petroleum ether, hydrogen-benzene vapor flame in the Linn a n'schen blower, in which the Oxygen is pressed into the flame under a pressure of 10 to 30 cm of mercury. Then burns the hydrocarbon completely close to the oxygen inflow (blue-green flame cone) and the large, almost colorless, rustling flame at the top shows only the spectrum of water vapor.

Spectrum III (Plate I) shows the decomposition of the spectrum of those burning with oxygen  
Hydrocarbons reproduced from my spectrum photographs.

1) According to L i v e i n g and D e w a r (Proceed. Royal Soc., London., Vol. XXX [1880], pag. 152) there are hydrogen and Carbon disulfide vapor, burned in air, no trace of the "hydrocarbon bands"; on the other hand there is hydrogen and carbon tetrachloride, burned in air, the hydrocarbon band (S w a n'sches spectrum), also carbon oxide + carbon tetrachloride, as well as a chloroform + hydrogen flame. The

visible and the ultraviolet spectrum.

Emission spectrum of the burning hydrocarbon (carbon or hydrocarbon bands). (Based on Hartl e y-A d e n e y's older standards.)

- 1) Spectrum of burning hydrocarbons (Bunsen burner or hydrocarbon-oxygen blower).
- 2) Induction sparks in dilute hydrocarbons (G e i s s l e r'sche tubes).
- 3) Band spectrum of the carbon in the electric flame arc.
- 4) Was observed directly with a Krü s'schen spectroscope in the luminous gas oxygen blower.
- 5) From here on, measure on the photographic negative.
- 6) Essence d o n c k obviously had the strong halo of this line, which runs towards the more breakable end, in the measurement (Middle of the line) included; hence the low wavelength.') The lightest line in the group.  
") Is very faint; a fourth, more breakable line, which is only found at Watts, could be from me in burning hydrocarbons

not be observed.  
Angstrom Liveing Kayser  
and Hasselberg Lecoq and Eder remarks  
Thalen Dewar stake

) I always observed these rather strong lines Violet

J in the spectrum of burning hydrocarbons. you form a  
separate group 4) in the whole

C band e

violet band e, to which the the

following group joins

1) Hasselberg observed a blurred light field in burning hydrocarbons, the greatest intensity of which was I-4367.

2) Lecoq evidently has the middle of the two opposite marked and photographed by me in the Bunsen flame  
Spectral lines measured.

3) This band was measured by Kayser and Runge in the electric flame arc.

4) This occurs strongly in the cyan spectrum (cyan + oxygen) as well as in the electric flame arc between carbon electrodes

Band is not particularly prominent in Swan's spectrum of burning hydrocarbons. In the electric arc of flame

the strong lines I-438, 437 and 436 are the edges of complex line bands. In the spectrum of burning hydrocarbons this became

Group measured by me for the first time. The character of the in the group occurring in the cyan spectrum is somewhat different than in the

Swan's spectrum, because in the latter case the continuous spectrum and the lines of the next group (from I-436 to 432) are strong

step forward. -If ammonia gas is present in the coal gas-oxygen flame, the lines I-438, 437 and 436 appear more clearly, likewise the yellow-green cyan bands.

3 \*

and Hasselberg Lecoq Watts and Eder remarks  
Thalen Runge

4359 6

4356 4

this group consists of a6 continuous  
4352

weakly luminous spectrum on which the 4348  
4

Lines stand out lighter. In the photographic

Negatives disappear with longer exposure 4344 .

2 violet

the lines that now appear black

4340 · 0 a dark background of reduced Silver

')

C-gang "

4335 7

4329 1

4324 · 8 single strong line

43 15 · 0 very strong line. Characteristic 4). The following 4309

4313 4311 4319 ")

Lines are initially sharp and strong and become 4306 6

gradually weaker towards the breakable end.

4299 · 2 The distribution is regular. At lower Exposure or low-burning bunsen

4290

4293 9

burner only the lines to, = 425 come to the 4285 4287  
6

Appearance; with long exposure or with intensification 4279

silver combustion in hydrocarbon acids fabric

blower, the lines extend to, = 481

from then on, with a narrow gap in the Spectro

\

graph these lines as more or less 4207 6

recognize clear double lines, the center of which is in

J in the adjacent table was measured.

1) If the exposure is too long, they disappear completely into the dark background; if the exposure is too short, they become foggy and immeasurable. ') Hasse Iberg assigned the position of the sharp edge against Roth; the gangextended at Hasse Iberg's observations bis, 4239, perceiving about ten lines.

3) A line-rich cyan band begins here, which K ays he and Runge measuredprecisely.

From the wavelength of this characteristic cyan band (beginning, 4216) shows that this cyan band (whichalso occurs in the electric flame arc between Carbon electrodes occurs) not with the above, from me with I; designatedcarbon band is identical.

4) This line forms the limit of this extremely characteristic band of carbonagainst the red side of the spectrum; then follows towards the less breakable end follow the single line, 4325 of the band s, towards the more breakable end of the spectrum in close order on the main line), 4315 of Volume I; the other lines of thistape. Line 4315 points towards the red end

a sharp edge turned towards the spectrum, towards the ultraviolet theygradually become shaded and it stand out on one

weak continuous spectrum from the lines recorded above (from, 4306 to 4185).

With long exposure or bright light sources

the continuous spectrum following the borderline appears so intense in the photographic negative that the first

3 to 4 following lines are no longer recognizable. With sufficient exposure,the boundary of the characteristic line moves over, 4315 towards

, 4316 before; in the case of briefly exposed plates, on the other hand, thecenter of the line is at 4310 or 4312.

Kayser

and Eder B e m e r k u n g e s 1)

Stanchion

at the beginning: a weak continuous spectrum

Ultraviolet 4047 x 3 very weak

4032 x 8 weak t) C band "I)4019 · 0

stronger J

1) The whole band, like the C band e and -0 · is shaded in the oppositedirection than the bands a., Ss, r, ö and ~;

for in the former the strongest edge of the band is turned towards theultraviolet, and the lines become weaker towards the red end;

with the latter, the reverse is true.

2) These lines appear only with difficulty in the ordinary Bunsen flame, on the other hand more easily when one is burning oxygen

Hydrocarbons blowing; the following lines also emerge in the Bunsen flame.bas visible and

the ultraviolet Spectrunl.

) I the following lines are difficult to stand out from (End of this segment against ultraviolet the dark silver deposit of the negative.

strong single line; characteristic

isolated characteristic final line

1) See note on p. 20.

2) This cyan band measured by Kayser and Runge does not seem to be identical with my band 1J (in the burning hydrocarbon), because in the latter the characteristic cannelled bands A 3883, 3871, 3855 (but especially the strongest cyan band , 3883) are not represented here, but only the isolated line), = 3872.6 with the starting edge of the second cyan segment ( $\lambda = 3871.5$ ) meets closely.

3) With the ordinary Bunsen flame only a foggy streak is noticeable here; if you increase the intensity of the light  
Blowing in oxygen so it dissolves in dr faint lines.

4) This band occurs only with very long exposure and fanning of the hydrocarbon flame with oxygen. The lines are regular distributed; the band becomes weaker towards the less breakable end and the lines gradually continue to stand in that direction

apart. At 3642 to 3634 there is a weak, continuous spectrum. The construction is analogous to that of gang 11

II. The spectrum of water vapor in the emission spectrum of burning hydrocarbons  
or the oxyhydrogen blower.

As early as 1852, Stokes found that the flame of burning hydrogen was fluorescent and therefore must be rich in ultraviolet rays 1).

1) S. Huggins: "Compt. rend. », 1880, p. 1455.

J. M. Eder.

Living and Dewar reported in 1880 (Proceed. Royal Soc., London 1880, Vol. XXX, pag. 498) that in the spectrum of the luminous gas and oxygen flame, as well as the oxyhydrogen flame, are  
show many lines between sun lines R and S.

In a second treatise<sup>1</sup> they gave a diagram of the main volume of this spectrum and reported that the same spectrum arises when the electric sparks (without condensers) between overturn over moist hydrogen, oxygen or nitrogen.

H u g g i n s 2) den investigated simultaneously with Living and De and independently of these Hydrogen burned in the air or with oxygen by photographic means.  
He found a large number of ultraviolet lines and determined their wavelength, which Numbers given in our table are.

Later, Living and De were concerned again with the spectrum of the oxyhydrogen flame

(Proceed. Royal Soc., 1882, Vol. XXXIII, pag. 274; Philosoph. Transact., 1888[2], CLXXIX, pag. 27) and

Careful measurements of the wavelengths along with the drawn and photographic plates of these Spectral recordings in partial recordings.

Living and Dewar used a spectrograph with a simple calcite prism and related the scale for the wavelengths of the water vapor spectrum to the iron spectrum; the scale was the fear of the sun. The measurements of Living and Dewar are very complete and extensive varies from  $\lambda = 426$  to  $\lambda = 2273$ ).

Deslandres also dealt with the ultraviolet spectrum of water vapor<sup>4</sup>); he brought water into a Geissler tube and filled it by evacuating the tube with water vapor, through which he let the electric spark strike. This also occurs

Spectrum of the oxyhydrogen flame on, however, soon becomes the same with lines of hydrogen and

Oxygen permeated. Deslandres gave only the wavelengths of a few main lines of the water vapor bands which are included in my table.

About the considerations of Deslandres, concerning the analogy of the general structure of the water vapor bands

with the absorption spectrum of oxygen (telluric bands A, B, C), as well as the

Analogy of the water vapor bands with the ultraviolet oxygen bands and the one linked to them

Consideration, reference is made to the original treatise, as I in my present paper do not elaborate on these relationships.

The reason why, in spite of the existing examinations by the spectroscopist mentioned, I again studied the emission spectrum of the oxyhydrogen flame and a new determination of the wavelength made was a multiple.

First it was for my investigation of the spectrum of burning hydrocarbons of interest in ascertaining whether those in the ultraviolet part of the light of the hydrocarbon flame occurring bands ( $H_2O$  only, ~ 'y of my table I) are completely identical to those of the pure burning

Hydrogen (oxyhydrogen blower), or whether perhaps individual groups of carbon lines in store the bands of water in it, which can only be done by re-measuring the spectra in question was to be decided. I also came across Prof. Grünwald's treatises on "Math

1) "On the Spectrum of Water", Proceed. Royal Soc., London, Vol. XXX, p. 580.

2) Compt. rend., 1880, Vol. XC, pag. 1455; also Proceed. Royal Soc., London, Vol. XXX, p. 576 (1880); in the latter

Treatise, Huggins's statements are more complete than in the first.

3) In Watts: "Index of Spectra" (1889) the table of the Living and Dewar is given incompletely in g-Dewarian numbers,

since several bands of longer wavelengths are omitted; it is therefore special to the original treatise (a. a. 0.) referenced.

4) Theses presentees a la faculte des sciences de Paris. I. Specters de Bandes Ultraviolet des Metalloides avec un faible dispersion (Paris 1888, near Gauthiers-Villars). Excerpt: «Compt. rend. », Vol. C, p. 854; «Anna l. Chemistry and Phys. " (6), XIV, 257 (1888).

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The visible and the ultraviolet spectrum.

matic spectral analysis of the magnesium in the coal "1) and via" spectral analytical detection of acidn of a new element »2) on that the same in his calculations on the rhythmic Relationship of the primary elements in their various forms of condensation to the water spectrum

the Huggins wavelengths of the water spectrum next to the Liveing-Dewar numbers put in the bill. - But those for the characteristic lines of the water vapor spectrum are correct from H u g g ins, Des 1 andres, Live in g and D e was not specified wavelengths sufficiently exactly match.

If it could now be shown from further investigations that the Huggins' numbers only more imprecise values of the same main lines of the water spectrum are than the more precise Liveing D

e w a r, then the former would be from the Grün w a 1 d'schen tables for mathematical spectral analysis

to be deleted and of course there would be gaps in the relevant places Enter the tables quoted.

Furthermore, it was important to me to obtain a coherent picture of the structure of the emission spectrum of the

To have water vapor, as such was not yet available 3). Indeed it was me with mine

Quartz spectrographs are able to produce such a coherent image of the mentioned spectrum

obtained, which is also reproduced in plate I, Fig. IV and V, in heliogravure; however, she suffered

Sharpness (especially in Fig. V) noticeable in reproduction; if in general in spite of themselves I owe the heliographic prints very satisfactory to the difficulties presented This is thanks to the friendly cooperation of the Management Board of Maschek im k. k. military-geographical Institute in Vienna, which carried out the heliogravures.

To get the result of my spectrographs of the ultraviolet water vapor bands of the oxyhydrogen flame,

as well as the hydrocarbon flame, note the following:

The emission spectrum of the blue Bunsen flame always contains in addition to Swan's coal spectrum

the main band of water vapor very clearly; the appearance of the nicely defined, off many lines of existing band spectrum is very remarkable, as the same inflames of relative at such a low temperature (like luminous gas with air in the Bunsen burner) has not yet been recorded.

However, even after 24 hours of exposure, only the main bands  $H_2O$  x and  $H_2O$  ~ emerge,

while the more breakable water bands (y and ~) only vigorously when oxygen is supplied to the Advance receipts come; The groups of lines are also pressed in when the hydrocarbons are burned

Oxygen (at a pressure of 20 cm of mercury) much sharper than it is with the ordinary Bunsen flame occur.

The spectrum of the oxyhydrogen flame is similar to that observed in burning hydrocarbons identical and I could not observe any carbon lines embedded in the water bands.

As for the wavelengths of the water vapor bands given by Huggins, so

a comparison with my measurements shows that they are not independent next to the Liveing-Dewar's numbers have to apply, but that the spectrum with an spectrograph is less efficient than mine or the Liveing Dewar's; leave it the lines measured by Huggins are undoubtedly in the Liveing-Dewar'schen, as well as in mine

Recognize tables.

The relevant ones, recorded by Prof. Grün in S's numbers due to the Huggins Special values of water vapor lines, which have just been mentioned, are therefore to be deleted.

The wavelengths of the water vapor spectrum determined by me are, as mentioned, on Hartley's related to the e y's wavelengths of cadmium, zinc and lead.

1) Meeting area d. kais. acad. d. Scientific, mathematic-naturw. Classe, XCVI. Vol. (December 1887), p. 1154.

~) Meeting area d. kais. d. Akad. Wissensch., Mathem.-naturw. Classe, XCVIII. Vol. (1889), p. 785.

3) Liveing and Dewar recorded the spectrum of the oxyhydrogen flame in several segments.

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The same applies to my measurements compared to the Liveing Dewar's Numbers, differences valid, which are due to the different choice of the comparison Spectra and the underlying

the wavelengths of the metal lines. Since Hartley and Adeney investigated Wavelengths encompass a large number of carefully examined metal spectra, which among themselves are completely

are comparable, a possible reduction of my numbers to other reference spectra is easy to carry out.



Emission spectrum of the water vapor in oxyhydrogen flames, as well as in burning ones  
Hydrocarbons. (Based on Hartle y-A den e y's older standards.)

Living Des-Huggins and Eder remarks! Andres  
Dewar

Water band "(·

(From this band of the emission spectrum of the water vapor I only  
determined those stronger lines, which in that Belithe duration of the  
action, which the water band ß

in all weak lines zu allowed to take pictures.  
Live in g and De was given weakest lines the  
table above is omitted.)

\* Weak line. t Very weak line.  
4 \*

J. M. Eder. The visible and the ultraviolet spectrum.

Comments on Mr. C. Bohn's treatise:  
«About flames and glowing gases».Of

J. M. Eder.  
("Journal for physical chemistry", November 1895.)

In the XVIII. Volume of the Journal of Physical Chemistry, p. 219, shared by Mr. C. B oh n  
his experiments on the spectrum of the luminous gas flame burning from the Bunsen lamp  
with which he made by means of the Te c 1 u'schen burner. The test results described in great  
detail  
partly contain information which my treatise: "On the visible and the ultraviolet emission spectrum  
of weakly luminous hydrocarbons (S w a n's spectrum) and  
the oxyhydrogen flame »(see pag. 1 of these treatises, as well as Table I).

In this treatise of mine, which seems to have remained unknown to Mr. B, I have  
some of his statements published earlier on the basis of my attempts at that time, others stand  
against it  
this information contradicts my observations. My spectral measurements back then were  
partly by direct ocular observations on the glass spectroscopic, as well as on the basis of spectral  
photographs  
by means of a quartz spectrograph, so that I not only see the visible Could examine the  
flame spectrum, but also the ultraviolet spectrum of the burning hydrocarbon  
first found.

Even then I succeeded in proving that the ordinary flame of the Bunsen burner, to which only so much air is supplied that that one does not burn brightly and one that is weakly blue

Has flame cone, gives the following spectrum: a weakly luminous continuous spectrum with embedded Swan bands. Even the upper one, almost colorless and extremely weakly luminous

Part of the Bunsen flame shows the Swan spectrum, but so faint that I can only see it

With the help of the Spectrum photographs by exposure for many hours, I was able to prove.

This upper part of the flame

shows mainly the water vapor spectrum, which of course can only be demonstrated in the ultraviolet

leaves. I managed to a. a. O. described in detail and by a heliographic table clearly demonstrated in my spectrum photographs, a separation of the spectrum of the blue flame cone,

which gives the Swan spectrum very strongly, from the colorless upper cone, which

the water vapor spectrum gives by blowing oxygen into luminous gas, benzene, petroleum ether flames

Etc.

My measurements of wavelengths gave the following results:

Rothe Gang 'I: (appears extremely weak in the Bunsen flare and only becomes when it is blown in

strongly visible from oxygen) consists of five lines: 'A = 6188, 6120, 6052, 6999, 5955.

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Ge 1 b e band  $\beta$ : A. = 5634, 5583, 5539, 5500, 5470.

Green band  $\gamma$ : A. = 5164, 5128, 5095.

Blue band  $\delta$ : A. = 4736, 4714, 4697, 4684, 4677.

Violet band  $\epsilon$ : A. = 4380  $\cdot$  4, 4371  $\cdot$  6, 3364  $\cdot$  4, 4359  $\cdot$  6, 4356  $\cdot$  4, 4352  $\cdot$  6, 4348  $\cdot$  4, 4344  $\cdot$  2, 4340  $\cdot$  0, 4335  $\cdot$  7, 4329 and the single line A. = 4324  $\cdot$  8.

Violet band  $\zeta$ : strong line, A. = 4315  $\cdot$  0, to which A. = 4306  $\cdot$  6, 4299  $\cdot$  2, 4293  $\cdot$  9, 4287  $\cdot$  6, 4282  $\cdot$  0, 4276  $\cdot$  4, 4269  $\cdot$  6, 4263  $\cdot$  4, 4256  $\cdot$  9, 4250  $\cdot$  7, 4244  $\cdot$  3, 4338  $\cdot$  2, 4232  $\cdot$  3, 4226  $\cdot$  2, 4220  $\cdot$  2, 4213  $\cdot$  9, 4207  $\cdot$  6, 4201  $\cdot$  8, 4195  $\cdot$  2, 4190  $\cdot$  0, 4184  $\cdot$  8 connects.

Ultraviolet band  $\eta$ : Initially a weakly continuous spectrum, then weak

Lines: A. = 4047  $\cdot$  3, 4032  $\cdot$  8, 4019  $\cdot$  0, 4005  $\cdot$  7; then getting stronger: A. = 3993  $\cdot$  9, 3982  $\cdot$  4, 3971  $\cdot$  8,

3961  $\cdot$  9, 3952  $\cdot$  5, 3943  $\cdot$  8, 3935  $\cdot$  7, 3927  $\cdot$  9, 3921  $\cdot$  3, 3915  $\cdot$  5, 3911  $\cdot$  3, 3906  $\cdot$  0, 3902  $\cdot$  4, getting weaker:

A. = 3898  $\cdot$  7, 3896  $\cdot$  0, 3893  $\cdot$  0, 3889  $\cdot$  8, 3884  $\cdot$  4, 3875  $\cdot$  6, 3877  $\cdot$  2, 3875  $\cdot$  7 and the single strong one

Line: A. =  $3872 \times 6$ .

Ultraviolet band D · (occurs only when the hydrocarbon flame is fanned with oxygen on): A. =  $3687 \cdot 0$ ,  $3677 \cdot 5$ ,  $3668 \cdot 6$ ,  $3663 \cdot 6$ ,  $3660 \cdot 7$ ,  $3657 \cdot 4$ ,  $3654 \cdot 0$ ,  $3650 \cdot 9$ ,  $3646 \cdot 1$ ,  $3642 \cdot 0$ ,  $3638 \cdot 0$ ,  $3634 \times 5$ ; then the strong line A. =  $3627 \cdot 4$ .

These figures of mine represent the type of the Swan spectrum more precisely than those Boh nian scale indications, apart from the fact that they also include the short-wave spectral regions.

In order to determine these figures even more precisely, I am currently in the process of sharing with Mr. E. Valenta

make a new determination with a concave grating, which is much more accurate wavelength measurements,

than those obtained with the prism apparatus of small dispersion allows. But even then when these wavelengths have been determined with the greatest possible accuracy by means of the grating spectrograph

However, the Swan spectrum is only poorly suited as normal light if one carries out optical determinations with characteristic types of light waves.

Mr Boh n says that with the sharp edges of the Swan spectrum, "quite good." Let determinations of the refractive exponent of three kinds of light be obtained, which is more convenient than that

Line spectrum of hydrogen. I cannot agree with this suggestion, because as for the Swan bands have been shown to belong to the type of band whose individual components widen unevenly on both sides, so that they have a variable brightness or gap width seem to change their position in the spectrum; for this reason the main lines of the Hydrogen's more accurate results if referred to.

Boh n's objections to the sentence "passed into the textbooks" (p. 227):

«That solids are continuous, gases and vapors discontinuous, at low temperatures

Giving band spectra, or line spectra at higher temperatures, are not entirely understandable to me; because first of all

Bunsen himself has occasionally shown in his investigations into the "Didymic spectrum" that solid glowing bodies can give a band spectrum and, secondly, Mr. Boh n turns against the "second part of this proposition". However, this latter objection would be fundamental nothing to say, but I have to speak out against the Boh n'sche motivation, because I consider them incorrect. The named says namely, «his communication lives», that burning Hydrogen (and carbon oxide) gas gives continuous Spectra. That is in this general version incorrect, for it is only valid for the visible part of the spectrum of the H-flame, whereas the same applies

shows an excellently defined, complexly constructed discontinuous spectrum, which, however eludes direct ocular observation, for it is known to be in the ultraviolet.

Furthermore, Mr. Böhner's remark (p. 229) is not applicable: that «only in the case of explosive (oxyhydrogen)

Combustion of the hydrocarbon; the band spectrum occurs. Mine in the one quoted earlier  
Treatise published photographic reproductions of the flame spectra show beyond doubt

Comments on C. Böhner's treatise: On Flames and Luminous Gases.

the appearance of the band spectrum in the usual Bunsen luminous gas flame; of course it's the same

Poor light, but clearly detectable objectively by means of spectrum photography.

I do not want to go into further details, but rather the ones given on p. 238

Turn to the "main results" of the paper in question.

Ad 1, where Mr Böhner says: «It is not correct that glowing gases and vapors always

give discontinuous spectra. With normal combustion they produce continuous spectra »,

the following is to be observed: the first movement is not new, but it is for the visible part of the spectrum.

correct. The last sentence has been re-established by Mr Böhner, but it is not applicable.

Because when the named says: "The gases and vapors usually give off combustion

Continuous spectra, "this contradicts the facts, for it is precisely those investigated by him

In the Bunsen burner, luminous gas flames always give the Swan and the \Vasser bands and

Lines. The further sentence Böhner's: "only in the case of explosive combustion do they provide band spectra"

falls automatically in this exclusive version in further consequence. The final sentence of § 1 (pag. 238):

«On the other hand I have (Böhner) when induction sparks pass through diluted gases and vapors

Preserving band spectra » naturally says the familiar and is applicable, as is point 2

on p. 238.

Ad 3. Regarding point 3 (p. 239), in which Mr Boh n declares: «It is not possible for him to have a specify a certain band spectrum of the carbon "and it hits" the mark, the less breakable edges of all carbon bands are sharp, the breakable ones are washed out, »not to, I notice the following: the non-existence of this alleged "mark" was recognized by me in my document mentioned at the beginning.

In my treatise it says: "Those known up to now, including those I found Bands of the Swan C spectrum can be derived from the structure of the lines exist, divide into two different groups.

-1. First group of C-bands, which against the

less breakable end to have the strongest lines and a sharp one in the same direction show strong edge, while the following lines, towards the more breakable end, gradually become weaker and follow one another at large intervals. Here: belong the bands  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$

and  $\sim$  -2. Second group, in which the arrangement of the lines and the shading of the bands

takes place in the opposite direction; here is the characteristic borderline of the band against the

more breakable end and this closes in the direction of the less breakable part of the spectrum shows a band consisting of numerous lines, in which the lines in the same direction to become weaker; at the same time the lines follow in towards the less breakable end ever larger distances. The bands  $\epsilon$ ,  $\zeta$ ,  $\eta$ ,  $\theta$  belong here. It is characteristic of these bands that that the strong end line turned towards the more breakable end is clear is isolated from the group of lines shaded towards the less breakable end, etc. ».

It is therefore not possible to determine the direction of the shading of the bands from an indicator speak in the Swan spectrum, but has several characteristics for certain groups, depending on the sharp edges of the bands, now turned towards red, now towards ultraviolet are.

On the phenomena of Pücker's tubes described by Mr. Boh n, which with CO, CO<sub>2</sub> and CH<sub>4</sub> are filled, I do not want to go into more detail at this point; these observations are very interesting and can only be discussed better when the relevant lines will be measured more precisely.

About the visible and the ultraviolet Emissions spectrum of the ammonia-oxygen flame (Ammonia spectrum).

Of

J. M. Eder.

(Presented at the meeting of the Imperial Academy of Sciences on November 3, 1892.)

In my investigations, "Over the visible and the ultraviolet emissionspectrum, weak glowing burning hydrocarbons and the oxyhydrogen flame »1) I was convinced that the characteristic lines and bands of such flame spectra in the violet and ultraviolet parts. It seemed interesting to me, including the emissionspectrum in oxygen to subject burning ammonia to a more detailed examination, provided that: to find characteristic new lines in the more frangible part of the ammoniaspectrum.

Right from the first preliminary tests I found this assumption confirmed.

About the ones I discovered

highly characteristic and well-defined bands in the violet and ultraviolet of the spectrum

I made a preliminary note of the ammonia-oxygen flame in the Imperial Gazette Academy of Sciences in Vienna from March 6, 1891 a communication.

These main bands and lines of the ammonia flame spectrum in the ultraviolet even have one far greater photographic brightness than the previously known mostly blurred lines in the visible spectrum, which the latter have hitherto repeatedly been the subject of observation, namely by Mitscherlich 2), Dibbits 3), Hofmann 4) and G. Magnanini 5).

From these determinations of the wavelengths of the lines and bands of the ammonia flame spectrum

the most detailed come from G. Magnanini, who averages the visible spectrum

of a Kruss spectroscopist (with two glass prisms of 60 °). However, subjugated this spectroscopist, like Dibbits and Hofmann, only covers the lighter part of the spectrum the investigation; direct observation is already uncertain in the indigo blue, and it is in the violet

With the low brightness of the spectrum in question, the lines either hardly or not at all

1) cf. page 1 of these treatises.

2) Poggendorff's Anna!., 1863, vol. CXXI, pag. 459. Also Kayser: "Spectralanalyse", 1883.

3) Poggendorff's Anna!., 1864, vol. CXXII, pag. 497. Also Kayser: "Spectralanalyse", 1883 and Watts: "Index of Spectra », 1889, p. 161.

4) Poggendorff's Anna!., Vol. CXLVII, pag. 92. -Kayser: a. a. O.

5) Atti della reale Accademia de lincei, 1889, quarta series, vol. V, 1st semester, p. 900.

The emission spectrum of the ammonia-oxygen flame.

visible and evade measurement. The study of this, as well as of the ultraviolet part, is only

possible with the help of the photographic method which I used for this reason in order to get a more precise knowledge of this strange spectrum.

While so far only about 70 lines in the visible spectrum from  $\lambda = 6666$  to  $\lambda = 4450$  known, I discovered about 240 new lines,  $\lambda = 5000$  through  $\lambda = 2262$ , so that the As far as we now know, over 300 lines of ammonia emissions, including but there are undoubtedly still multiple unresolved bands consisting of numerous lines should exist.

The applied quartz spectrograph.

Although the quartz spectrograph I used (which is a Cornu'sche mountain crystal prism of  $60^\circ$ ) already described in detail in the earlier cited treatise in the "Memoranda" I still feel compelled to supplement that description retrospectively prompted by several inquiries regarding some details of this apparatus.

Fig. 12.

Fig. 12 shows the external view of the spectrograph, with the Schumann's camera and

Cassette device; a is the partial drum of the collimator gap, which can be regulated by a micrometer screw,

b the collimator tube, its position in relation to the prism through a screw device at c can be changed. The collimator lens (mountain crystal) can be adjusted using the drive (d).

The housing (e) contains the Cornu prism and at f there is the drive for the rock crystal lens, which the spectrum image is in the photographic camera (g) on the next h inclined plate throws, which is located in the known manner in a cassette.

J. M. Eder.

The camera consists of a long wooden box (g), the tapered end of which is the track which carries a cassette that can be moved in parallel by means of two drives and toothed racks.

The career is for

Longitudinal direction of the box very inclined. The angle it includes with the center line of the box,

is about  $25^\circ$ . The camera can be rotated around a pin that is below the cassette track is mounted on a sturdy arm of the cast iron base of the spectrograph. The elongated geometrical axis of this peg coincides exactly with the vertical center line of the photosensitive

Side of the photographic plate together; at the same time, the optical axis intersects the camera lens.

The pivot axis, the direction of travel of the plate and the refracting edge of the quartz prism are parallel.

As a result of this peculiar arrangement of the tenon (z), the center of the plate remains once it is in focus, also still in focus as soon as you turn the camera and at the same time the

Fig. 13.

$I \sim - + \sim \sim = iE \sim \sim \sim - "$ :  $\cdot =$ :  $\sim \sim$ :  $\sim \sim J = \sim ,$ ,  $f_u = G$

"

~

The inclination of the plate to the lens axis changes. Setting the camera to a specific angle is necessary if the spectrum is to appear equally sharp in all its parts. The angular mobility of the camera includes  $10^\circ$  and the tilt

Fig. 14.

The angle between the lens axis and the plate can be anything between  $20^\circ$  and  $30^\circ$   
»----- RR: '= --- c-g can be changed.

Fig. 13 shows this, devised by Mr. V. Sc human n in Leipzig, extremely advantageous facility seen from above. The rotation of the camera

$0 / dt.dw \ dr, \ JrJ, \ siin$

TIWllmit

takes place at z. The objective (f) is fixed to the housing for the double prism

iID'Camera ..

appropriate. A fixed metal arch (i) excludes external light.

14 shows in a side view how this metal sheet (i) is light-tight and yet movable is connected to the camera (g).

For the rest I have to the description given in my earlier treatise of that of nothing to add to the apparatus I used.

Production of the ammonia-oxygen flame and the comparison spectrum.

The spectroscopists mentioned, who examined the visible spectrum of the ammonia flame, burned gaseous ammonia with oxygen and used the resulting pale yellow flame. Monitoring. I also followed the same process, but had to be extra careful to achieve a long lasting ammonia flame as bright as possible, because the same for my purposes during



an exposure time of approximately 6 to 12 hours had to last approximately constant. The fainter ones

Bands of the ammonia spectrum only entered after a long exposure time. Sufficiently strong photographic image, which clearly shows what is necessary to measure the lines possesses.

The emission spectrum of the ammonia-oxygen flame.

A constant and sufficiently bright ammonia-oxygen flame can be found in the following way. Achieve: An intimate mixture of slaked lime and chlorammonium is created in a spacious glass flask

slowly warmed up in the sand bath and washed the escaping ammonia gas in water.

The drying of the gas did not seem to me necessary for the experiment described here, because

When the ammonia is burned, water vapor forms anyway and the water bands in the spectrum are inevitable.

The ammonia gas is led to a T-shaped glass tube, into which, on the other hand, a slower one

Stream of hydrogen gas enters.

The hydrogen is developed by means of zinc and sulfuric acid and purified with a silver sulphate solution

and then passed through several Wü 1 ff bottles filled with strong aqueous ammonia, thereby taking ammonia gas with him.

This mixture of ammonia gas and hydrogen gas<sup>1</sup>) is transferred from the T-pipes into a line

led to a n'sches "oxyhydrogen blower" and ignited. The spectrum of that pale yellowish flame shows a not particularly vivid ammonia spectrum. However, the brightness of the spectrum becomes noticeable

bigger as soon as you let oxygen in. It then separates the flame into an inner one, pretty much

bright, pale yellow cone and an abundant, upper, almost colorless part of flame (mantle).

Leaves

if too little oxygen is admitted, both parts merge, but the flame is lost in the process

in brightness; at the right With oxygen supply, the inner yellow cone is approximately  $\frac{1}{2}$  to 1 cm high

too much oxygen, however, the yellow cone disappears almost completely and the flame shows no ammonia spectrum more.

It should be mentioned right here that only the spectrum of the inner g e 1 b e n K e g e 1 s of the ammonia-oxygen-

F 1 a m m e emits the characteristic ammonia spectrum, while the almost colorless one outer coat gives the water vapor spectrum, which however only in the spectrum photography

of the ultraviolet is detectable, but remains invisible to the eye on direct observation.

The same phenomenon prevails with this flame as with the spectrum of the Bunsenian Luminous gas flame, with which I also demonstrated 2) that the Swan coal spectrum appears most clearly in the inner blue flame cone, while the outer almost colorless Part only gives the water vapor spectrum.

The emission spectrum of the in oxygen discovered by me and described in more detail below burning ammonia are always the characteristic ultraviolet bands of the water vapor spectrum (Emission spectrum) more or less added. Since I have this latter Spectrum but in my above-cited treatise in the "Memoranda of the Academy" and precisely described had measured, it was the precipitation of the characteristic spectral lines associated with ammonia and bands from those of the water vapor spectrum are not difficult.

To determine the wavelengths of the lines of the ammonia spectrum, I used this spectrum on the spark spectrum of an alloy of zinc + cadmium + lead 3). For a better overview and to control the values I have given, I divide those wavelengths of the metal spectrum. with which I have used in the reduction of the observed and measured lines of the ammonia spectrum.  
put in the bill.

- 1) Ammonia gas + hydrogen burns more evenly in the oxyhydrogen fan than. Ammonia gas without the addition of hydrogen.
  - without the spectral phenomena differing in any noticeable way. 2) A. a. 0.
  - 3) This spark spectrum of the metal alloy was photographed in the middle of the ammonia spectrum (cf. enclosed table), so that the position of the lines above and below could be read off.
- 5 \*

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36

Cd 5085 Thalen

Zn 4924

Zn 4911

Zn 4813

C 4799

D

Zn 4721

Cd 4677

Air 4629 Hartley & Adeney 1)

Air 4446

Air 4415

Pb 4386

Pb 4245  
 Pb 4058  
 Air 3995  
 Air 3919  
 Air 3749  
 Pb 3739  
 Pb 3683  
 Pb 3639  
 Cd 3611 8  
 Cd 3609 6  
 Pb 3573  
 Cd 3466 8  
 Cd 3465 . 4

Air 3437 . 0 Hartley & Adeney  
 Cd 4302 . 9th  
 Zn 3344 4  
 Zn 3301 7  
 Zn 3281 7  
 Cd 2747 . 1  
 Zn 2711 5  
 Pb 2613 . 4

"

Zn 2607 6  
 Cd 2572 . 2  
 Zn 2557 3  
 Zn 2526 3  
 Zn 2521 3  
 Zn 2514 7  
 Zn 2490 4  
 Zn 2485 9  
 Pb 2475 7  
 Cd 2469 . 3

"

Zn 2441 6  
 Zn 2427 . 0  
 Pb 2393 7  
 Cd 2329 . 5th  
 Cd 2313 6  
 Cd 2265 2)

Description of the emission spectrum of ammonia.

When examining the emission spectrum of the ammonia-oxygen flame, the superiority occurs of the photographic method. This is not only true --'-- which goes without saying is for the ultraviolet, but also for those colors of the spectrum which are direct Observation with the eye are accessible, namely in blue and purple. It goes from this Comparison of the direct spectroscopic readings by D i b b i t s, Hofmann and Mag n an in i

with my spectrographic results obtained by photographic means (see later), where the latter make many more lines.

My photographs were taken partly on erythrosine-bromide-silver gelatine plates, partly produced on high-sensitivity pure silver bromide gelatine plates; the former recordings extend to yellow, the latter to green 3).

The red, yellow, and green lines are from Magnanini with satisfactory accuracy measured, while for the blue and violet bands only those of the photographic method would like to apply.

1) The accuracy of the measurements of this band only extended to one Angström'sche unit, which is why I also give the Hartley-Adeney numbers only to four digits.

") For this cadmium line, a value rounded down to Eine Angst Roman's unit was used because the The accuracy of the measurement of the related last ammonia band was no higher.

3) The heliography of the ammonia spectrum shown on the enclosed table is based on a photograph  
Silver bromide gelatine and only reaches the green, on the other hand the ultraviolet areas are clearer than mine  
Erythrosine plates.

The emission spectrum of the ammonia-oxygen flame.37

The emission spectrum of the ammonia gas burning in oxygen shows the following characteristics  
Construction:

1. A main band (x.) Of greater wavelength, which extends from Roth to the beginning of the  
~

Ultraviolet ers extends and consists of many lines or bands, some of which are sharper, some of which are faded;  
they do not show any noticeable regularity.

2. A second (only discovered by me) highly characteristic, consisting of sharp lines and regularly arranged band, which has the greatest photographic light effect in the whole spectrum comes to. The strongest line of this band (~) has a wavelength of  $\lambda = 3359$ , the second strongest  $\lambda = 3370$ ; to the right and left of these lines apparently a system follows in regular distribution of fine lines; the type of gang  $\beta$ , as well as the following main bands can be identified by the the following raw sketch 1) illustrate (Fig. 15), while a more detailed picture is the heliographic

3. On the more breakable side of the ammonia spectrum, five analogously built, one another appear very similar (also new) bands, which have their sharp edge against the less breakable End and in the other direction in very many, close to each other, quite a lot regularly grouped fine lines let dissolve. The adjacent sketch yFig. 15. to 'fl gives a casual picture of the

Gang (o :)  
on the one hand and cd on the other

```

111111111111 111111111111111111 111111111111111111 1111 11111 1111 1111
111111111111 1111 1111111 1

```

shaded towards the more breakable end  
Spectrum meets which  
might dissolve into fine, dense lines. There are many fine lines from the line d  
clearly visible. Next to band (13) is band,; the brightest, followed immediately in terms of  
brightness  
the bands 0 and (, then  $\gamma$ , then  $\gamma' 1$ .

has a distant resemblance in that both homologous bands gradually weaken will repeat and thereby to a certain rhythmic structure of the whole series the gangs point out. However, the ultraviolet bands are in the emission spectrum of the water vapor on the opposite side more shaded than with ammonia, i.e. the bands  $\gamma$ ,  $\beta$ ,  $\epsilon$  ;  
~ " f]

in the ammonia spectrum have their sharp and stronger edge towards the less breakable end directed and shaded towards the more breakable end; in the water vapor spectrum (band I, f, y, 3) the opposite is the case. Furthermore, the spectrum of ammonia extends much further towards the more breakable end than the spectrum of water vapor 2). All of them are also distinguished by six ultraviolet, very linear ammonia bands  $\beta$  to  $\gamma$  through a much more regular one

Build in relation to the water vapor spectrum. That the visible ammonia band is .. but irregular and is partially blurred, I have already mentioned.

- 1) See indicator d. kais. acad. d. Wissensch., Vienna (mathem.-naturw. Cl.), March 5, 1891, No. 6.
- 2) In both cases we are talking about the flame spectrum in the oxyhydrogenblower.

J. M. Eder.

In the following I divide the wavelength of the lines I have measured in the emission spectrum the ammonia-oxygen flame and add that of Lecocq de Boisb for greater clarity. I have also added the wavelengths determined by Hofmann and Magnanini in the visible spectrum. It is noteworthy that the wavelength determinations of the researchers mentioned in the Roth,

Yellow and green match satisfactorily, as well as most of them are blurred of these groups is possible. It is, however, very remarkable that the observation by direct reading on the spectroscope becomes very uncertain even in the blue; I found a whole series clearer enough

Lines on my Spectrum photographs in the blue, which the earlier observers escaped while the violet and ultraviolet bands I found are all new. The accuracy of my wavelength information is in the ultraviolet much more accurate than those in the less frangible parts of the spectrum because, on the one hand, the lines of the spectrum examined by me in the

the former case are better defined and, on the other hand, the dispersion of my spectrograph in the ultraviolet

is much bigger. It goes without saying that the lines of the emission spectrum are listed below

of the burning ammonia the elimination of the simultaneously occurring water vapor lines, which the

to partially enforce the former spectrum, was undertaken on the basis of my own previous investigations (memoranda of d. kais. acad. d. Science in Vienna, 1890). On the heliographic

Reproduction of the ammonia spectrum (Plate II, Fig. 1) one can clearly see the ammonia bands

,  $\gamma$  to  $\epsilon$ , together with the water bands ( $\delta$  and  $\eta$ ; right through is the comparison spectrum of an alloy

Photographed of cadmium, zinc and lead (spark spectrum). Unfortunately in the heliographic reproduction the subtleties of the delicate line structure of the individual bands have been lost, so that

our heliogravure gives only an imperfect picture of the spectrum in question.

Table of the wavelength of the lines in the emission spectrum in the ammonia-oxygen flame.

(Expressed in Angstrom units.)

Lecocq

1 Dibbits 1) Hofmann 1) Magnanini Eder

de Boisbaudran 1

1 1

Remarks

..

Ammonia band a.

-

} foggy line

-

6666

Line, foggy against purple

blurred blurred line

the band consists of many immeasurable lines sharp

line

} Line, out of focus towards the breakable end this band

forms a series of lines whose intensi

ity diminishes against purple

)> strong line

)

Ties, difficult to break into lines

near this line (against purple) is one fine line

this band consists of lines, foggy against red indistinct

539-527 534 5339 -5303 boundaries of a band which is of very weak

5252 527 -524 518-526 5270-5262

Lines is fulfilled this band consists of two lines, which gradually 5253-5242) borrowed to be foggy

523-517 5230 foggy

519-516 5212-5172 Band not resolvable in lines 5166

514 5156 foggy

513 5127-5123 foggy against the more breakable side 5115-

5108 foggy on both sides

508 507-502 5084-5072 5079 Center of the broad line

500-492 5072-5020 5007 · Line narrower than the previous one 592-472  
498 4995 -4955 4984 middle of a fairly broad line

496-495 4966  
4923 4924  
488 -485 4895  
4878 -4864 {  
4869  
4840 4839  
480-479  
4789-4774 ' ) {  
4785  
4777  
} Boundaries of a wide strip  
;; j "4747 ii3  
470-469 4722 wide strips  
467-465 4678  
4662  
4647 (?) 4641  
461 459  
4620  
4566

1) Magnanini declares the bands from 4789 to 4492 to be unclear and the boundaries of the same to be found uncertain. On my Spectrum photograph the course of the bands can be seen very well.  
d

This band is more luminous than the previous one; it is more luminous than numerous lines of existing tape

continuer

the bands 1, 0, S and r ;. The line b follows a against the break is; the latter

stands out on one

barer end of shaded band; a and e are isolated.lich with

gradually weakening con

traces of

continuous spectrum.

If you compare the numerous bands I found in the ultraviolet emissionspectrum of the ammonia-oxygen flame (including the bands in the visible spectrum), there is none 1 e i



Correspondence with the emission spectrum from hydrogen or nitrogen in the Geissler's Tubes.

It is the spectrum of the ammonia-oxygen flame, the compound spectrum of ammonia, which is analogous to the spectrum of the water vapor in the hydro-oxygen flame. The same thing

The spectrum of compounds of ammonia seems to appear when one looks at the electric spark

The emission spectrum of the ammonia -oxygen flame.

Let aqueous ammonia be tested. Lecocq de Boisbaudran ("Compt. Rend.", Vol. CI, pag. 43 1) found

namely, in the spark spectrum of aqueous ammonia, the strongest lines of the flame spectrum, what.

I can confirm on the basis of my own experiments. Emission

spectrum of amines, which burn in oxygen.

Although G. Magnanini (op. Cit.) Already described the flame spectrum of ethyl and trimethyl amine

(burning in oxygen) and found that no other spectrum besides the

If you see and the ammonia spectrum appeared, I repeated the same experiment because

Magnanini had not brought the ultraviolet into the scope of his research. It seemed to me namely not impossible that the flame spectrum of burning amines in the ultraviolet has a characteristic

Would show behavior. Therefore I burned gaseous ethylamine with oxygen and photographed the spectrum of this flame. The spectrum photograph showed three spectra stacked on top of each other:

1. See the spectrum of burning hydrocarbons.
2. The ammonia spectrum (but only in the main band [j]) \_
3. The water vapor spectrum.

I could not perceive the appearance of any new characteristic band or line, hence I conclude that the oxygen-burning amines are not peculiar to them. Give emission spectra, but only show the three mentioned spectra as components.

1) Also «supplement to the Annales de Chimie et de Physique», 1886, p. 171.6 "

About the usability of the spark spectra different metals to determine the wavelength in the ultraviolet

1).

Of J. M. Eder.

(Presented at the meeting of the Imperial Academy of Sciences on December 15, 1892.)

Orientation in the ultraviolet parts of the spectrum is sometimes difficult if one does not have very characteristic spectra, the lines of which are sufficiently evenly distributed, as reference spectra and there were different reference or orientation spectra by different spectroscopists used.

In order for my research on the wavelength of the new ultraviolet I discovered lines in the Swan spectrum, as well as suitable reference spectra in the flame spectrum of ammonia I had, on the basis of earlier attempts, an alloy of equal parts cadmium and zinc and lead chosen.

The choice of suitable light sources, be it for the purpose of producing reference spectra or to study various absorption phenomena in the ultraviolet, appeared to me for my other works of such importance that I have recently included this subject in the field of my experiments and produced a number of different spark spectra, some of them very rich in lines, which I in

· Their entire course from the visible (yellow, green, blue, violet) part to the extreme ultraviolet by means of my quartz spectrograph 2) on erythrosine-bromosilver gelatine plates 3), their sensitivity from the external ultraviolet to against incidentally  $\lambda = 6000$  Angstroms, photographed, to one

To gain an overall picture of the distribution of the energy of the spectra.

It also seemed to me the inclusion of some spectra from other light sources of interest; especially from Drummond's light, magnesium and electric arc light, compared to the solar spectrum, as all of these light sources are often used for spectral experiments and I mean their usefulness for had to try out test series.

1) With reference to the spectrum of sunlight, Drummond's, magnesium and electric arc light.

2) cf. page 1 of these treatises.

3) "On the spectral behavior of the erythrosine-sensitized bromosilver gelatine plates" (together with the illustration of the photographs of the solar spectrum produced by means of such plates » (see Eder: Sitzungsber. d. kais. Akad. d. Wissensch., mathem.-naturw. Cl., Vol. XCIV [2. Abth.], 1886).

About the usability of the spark spectra of different metals. Spark spectra of metals.

The idea is obvious to use such spectra as comparison spectra, which are very many have even lines that are close to one another, as is the case, for example, with

Spark spectrum of iron, nickel, cobalt and tungsten is the case. Namely, if you are new  
If the spectra to be examined relates to this, then the interpolation errors are in determining the  
wavelengths

very low; on the other hand, it is extremely difficult in the prismatic spectrum of  
moderate dispersion in the linear spark spectra of iron, cobalt, nickel or tungsten  
or similar metals with certainty to recognize characteristic lines as reference lines. this  
shows

a look at the spark spectra shown in plate II, which heliographic reproductions one  
The number of my Spectrum photographs are 1).

Orientation can be much safer than by means of the above-mentioned linear spark spectra  
by means of the cadmium and zinc spectrum. The overall picture of these is often used as a  
reference spectrum

The spark spectra used (quartz spectrograph) are shown in Plate III, FIGS. 1 and 2. On our  
plate are

the sometimes common M as a numbering of the cadmium lines (from No. 2 to No. 26)  
in addition to the wavelengths of the characteristic metal lines. As is well known, the cadmium  
spectrum

in the districts  $\lambda = 4677$  to  $3609$  (No. 9) and on the other hand between Cd No. 17 to 18, as  
well as

between Cd nos. 18 to 23 there are large gaps on characteristic lines, while the most breakable  
one

Partly well oriented by the Cd line nos. 23 to 26. There are the following in particular  
Lines with the adjacent \ Vellenlengths 2) into consideration:

Yellow Cadmium Line (No. 2)  $\lambda = 5379 \text{ \AA}$  .. f

Cd (No. 3) 5338

run I Cd (No. 4) 5085 5)

4799

{Cd (No.

Blue Cd (No. 6) 4677

Cd (No. 7) 4416

f3612

Cd (No. 9)

f 13610

(3467

Cd (No. 10)

j 13465

Ultraviolet (No.

11) 3403

r 3252

3250

Cd (No. 12). roo

Cd A = 3133

Cd 2980

Cd 2880

Cd 2836

Cd (No. 17) 2748

Cd (No. 18) 2572

Ultraviolet

Cd 2469 2314

Cd (No. 23)

Cd (No. 24)

22661

Cd 2241 4)

Cd (No. 25) 2195

Cd (No. 26 3) 2147

1) The exposure time of this and the following spectrum photographs reproduced in the plates was about nine

Quartz spectrographs, a fame of the greatest kind (with three L e y den er bottles) and fine-grained bottles

Erythrosine -Bromosilver Gelatine Plates:

for Mg sparks. . . 1½ minutes (gap = 0 023 mm)Cd, Zn,

Pb, Tl. 20th

Sn. .... 30th

Cu, Fe, Ni, Co. 40

2) Since this is only about the orientation of the metal lines, which are particularly useful for measurement purposes, so are

the wavelengths are only given with four digits, while in my measurements in the spectrum I always put five digits into the

Invoice were included.

3) Numbered after Co r n u.

4) These four Hart 1 e y numbers are too high so that I did not use them, but the K a y s e r numbers

Selected 2144 x 5, 2194 x 7, and 2239 x 9 as the starting point.

J. M. Eder.

These most important of the cadmium lines are easily accessible using the accompanying table to find. The yellow cadmium line (No. 2), then the green lines Cd (No. 3) and Cd (No. 4) appear in the photograph (with the aid of the quartz spectrograph) only after extensive exposure; also

Cd (No. 5) and Cd (No. 6) emerge clearly after 20 minutes of exposure; but with the ultraviolet Cd lines of Cd (No. 9) appear by far the strongest in spectral photography started. Some gaps in the distribution of the ultraviolet lines of the cadmium spark spectrum.

fill in the main lines of the zinc spectrum. This goes with the tour of the heliographic reproduction of the spectrum photograph of the zinc sparks (Plate III, Fig. 2) immediately and becomes  
 can be seen in more detail from the following listing of the characteristic zinc lines. The  
 Also in our figure, the main Zn lines are: Green Zn).

= 4924

4912

r Zn

┘ Zn 4810

Blue | Zn •. 4721 5

Zn 4679 6

Zn 33441

Zn 3302!

Zn 3282

Zn 30761\_

Zn 3072f

Zn 3035

Ultraviolet Zn

Zn

2801}

2770

Zn 2755

Zn 2712

Zn 2684

Zn 2657

Zn 2608

Zn 2557

Zn

). = 25261

Zn 2521

Zn 2515 f

Zn 2509;

Zn 2501 '

Zn

2490}

Zn 2486,

Zn 2442

Zn 2427

Ultraviolet Zn

2419

Zn 2349

Zn 2138

Zn

2104}

Zn 2102

Zn (No. 27 1) 2099

Zn (No. 28) 20631

Zn (No. 28) 2061f Zn

(No. 29) 2024

Of these zinc lines, the green and blue lines are good additions to the cadmium lines; the same is true of many ultraviolet Zn lines.

Nevertheless, the cadmium in combination with zinc provides usable orientation spectra which, in particular in the more breakable end of the ultraviolet have sufficiently numerous characteristic lines, — a well-closed reference scale is only obtained after including the lead-spark spectrum across the whole spectrum.

The spark spectrum of the lead contains clearly recognizable lines in yellow, green, blue and violet, as well as, several very distinct lines in the districts from  $\lambda = 4386$  to  $3573$ , which fill the large gap in the line-spectrum of the cadmium-zinc fill in. The lines of the lead spectrum are only obtained, however, sufficiently clean of oxide bands if the electrodes are brought quite close to each other and they are in front of each other cleans the lead oxide deposited on it each time it is used; also the induction current must (Ruhmkorff) a very strong and reinforced by several Leydener bottles. Then you get easily the main lines (see Plate III, Fig. 3):

1) Soret numbering.

About the usability of the spark spectra of different metals. 47 Yellow Pb) . — =

5607 Pb. ,) . — = 2822

Green Pb 5373 Pb 2801

In digo Pb 4386 6 Pb 2663

Pb 4245 Pb 2613

P

b

P

b

(4062 14058 1)

Pb

Pb

257

6

2562

Pb 3738 x 9 Pb 2476

Pb 3683 ultraviolet Pb 2446

Pb 3639 Pb 2444

Ultraviolet Pb 3573 Pb f2411 Pb

3176 Pb \ 2402

Pb 3137 Pb 2394

Pb 3043 Pb 2248  
Pb 2949 Pb 22041  
Pb 2872 Pb 2170 ()  
Pb 2832

For the reasons mentioned, I decided to produce a comparison spectrum by means of a Alloy of equal parts cadmium, zinc, and lead, which is a very well-defined band of the favorably distributed main lines of these metals. In this comparison spectrum, I have that from me examined (a. a. 0.) the hydrocarbon spectrum, as well as the absorption spectra to be described later from glass, the emission spectrum of the burning ammonia gas and so on (see Plate III, Fig. 1).

In some cases it may be desirable to compare the spark spectrum of the magnesium to be used, which Cornu in particular drew attention to 3). The magnesium spark is although poor in highly breakable ultraviolet rays, which are <2776, but a number of green, blue and ultraviolet lines (including several triplets) are highly characteristic (see Plate III, Fig. 4).

.. {Magnesium

Green Mg. ..  
Mg  
Blue Mg  
Indigo Mg  
Mg  
M  
g  
M  
g  
M  
g  
Ultraviolet MgMg  
M  
g  
M  
g  
M  
g

A = 5183} ". " " Hofec '

5172 see line

5167 b1> b2, bs

5704  
4481

r838

3832  
3829

f 3336

3332  
13329

r096

3092  
3090

1) Of these neighboring lead lines is Pb,  $\lambda = 4058$ , the Mg.  $\lambda = 2790$

Mg. 2928

Mg. 2914

Mg. 2851

Mg. 2802

Mg. 2797

Ultraviolet Mg.  $\lambda = 2794$  Mg.

L2790

Mg. 2782

Mg. 2780

Mg. 2779

~ Ig. 2777

Mg. 2776

decidedly stronger and more characteristic. In vV a t ts: «Index

of Spectra »(1889) is mistaken and called this lead line the weaker one.

2) Correct:  $\lambda = 2204 \cdot 3$  and  $2170 \cdot 0$  using Kayser's numbers.

3) Cornu gives a detailed description of the use of the Mg spark spectrum for the study of spectral and interference phenomena (Eder: "Yearbook for Photography and Reproduction Technology", 1891, pag. 183).  
)

J. M. Eder.

Of these magnesium lines, the green and blue lines appear on the quartz spectrograph only after prolonged exposure. The indigo blue Mg line 4481, as well as the line  $\lambda = 2851$ , which is a

of the most intense lines of the magnesium spark spectrum and the quadruple line group of  $\lambda = 2802$

up to 2790 are very well suited for orientation because of their conspicuous arrangement 1) (see Plate II,

Fig. 4); What is remarkable is the property of the Mg line 2851 that it is extremely light so-called "inversion" suffers, whereby the light line surrounded by dark edges denotes makes a false impression of a double line; something similar occurs with the quadruple band),  $\lambda = 2802$

a (see footnote). It is also noteworthy that the photographic effectiveness of the magnesium spark

is extraordinarily large. For example, while with my quartz spectrograph (see p. 33) the

Cadmium and zinc spectrum require an average exposure time of 10 to 20 minutes, thus the Mg spark spectrum only needs an exposure time of 15 seconds to get around the main lines



(2936 and 2928 mg, as well as 2802 to 2790 mg) to be given; exposure for 1 to 3 minutes

There are already numerous strong lines appearing and some of the main lines are already beginning to become strong broaden and appear partly reversed.

Sometimes I also use the Th a 11 ium spark p e c t rum with success to compare, which is shown in panel II, Fig. 5, and by the regular distribution of a large number of main lines about the ultraviolet is noticeable. The following Th a 11 iumLi are used for measurement purposes never n into consideration:

Green thallium 'A = 5350 TI

4110

TI 3932 7

TI 3776

TI f3529TI

I3519 TI

3381

TI 3229

TI 3091

TI / 2920 8 TI

I2918

Green TI i. = 2825 TI

2767

TI 2708 6

TI 2580

TI 2530

TI 2452

TI 2380

TI 2299

In the thallium spectrum there are no characteristic lines in the extreme ultraviolet, relationally the TI lines of 'A <22 ~ 9 are very poor in light, so that measurements in the most fragile ultraviolet the Cd-Zn spectrum or the like cannot do without.

Some have recommended the Z in the n-spark spectrum as the reference spectrum; Plate III, Fig. 6, shows the distribution and relative energy of the tin lines. I prefer the cadmium-zinc-lead alloy, however in front. However, as soon as you use the spark spectrum of the tin in the direction mentioned the following lines come into consideration:

Blue Sn) .. = 5524

f tin 'A = 5589

Yellow I

r Sn 5745

Sn. 5563

Ultraviolet {I Sn

3352

Blue Sn 5584

1) This quadruple band of the magnesium spark spectrum is extremely intense.

It is noteworthy that two of the

brightest lines of this band very easily undergo an inversion and therefore appear doubled by the sharp, bright,

reverse line is surrounded by dark borders; Co r n u first referred to this phenomenon («Archive des sciences

phys. et natur »., July 15, 1879).

•

About the changeability of the spark spectra of different metals. Sn 'A = 3330

Sn 3283

Sn 3262

Sn 3174

Sn 3033

Sn 3008

Sn 3862

Ultraviolet Sn 2848

Sn 2839

Sn 2181 3

Sn 2706

Sn 2660

Sn 2658

Sn

26451

Sn 2643)

Ultraviolet

Sn). = 2632

Sn 2571

Sn 2595

Sn 2429

Sn 2422

Sn 2355

Sn 2317

Sn 2288

Sn 22701

Sn

2269J

Sn 2267

Sn 2247

Sn 2210

Sn 2194  
Sn 2151

One will find these lines easily from the attached heliographic figure. How

one sees that the tin spectrum of  $\lambda < 3352$  is rich in well-defined lines, but which fewer are characteristic, as the lines of the Cd-Zn-Pb spectrum, which the latter incidentally also requires shorter exposure time.

The spark spectrum of copper is more difficult to develop than those mentioned above; it is still

less light than the tin spectrum, its main lines stand out less clearly and they mix more air lines, especially in the less frangible part of it. First drop from  $\lambda < 3307$  more abundant main lines of the Cu. These are in particular:

Copper.  $\lambda = 3307$  Cu

3273

Cu 3247

Cu 2769

Cu 2599 7)

~

Cu 2958 (J

Cu  $\lambda = 2545$

Cu 2370

Cu 2295

Cu 2277

Cu 2136

Cu 2103

These lines are also indicated in more detail in Plate II, Fig. 7; Incidentally, there are numerous lines from the breakable ultraviolet in the copper spark spectrum.

There are also the very linear spark spectra of iron, Nickel and Kobalt which have been drawn into the range of these experiments, especially with regard to their usability as light sources for studying the absorption phenomena in the Ultraviolet. Like from the In Plate III, Fig. 8, the published spark spectrum of iron emerges, the district indicates from incidentally

$\lambda = 3500$  bis),  $\lambda = 3000$  has a noticeably lower energy than the region from violet to casual),  $\lambda = 3500$ ; only with longer exposure does the spectrum image appear very linear in this area to the fore.

The region from about  $\lambda = 3000$  to  $2300$  has a very strong effect on silver bromide gelatine and shows a tightly closed line band. But since the energy of the iron spectrum is in the region of  $\lambda = 2300$

decreases fairly rapidly and the lines of smaller wavelength are only weakly effective, it appears

the iron spectrum for the study of absorption phenomena, especially in the region of  $\lambda < 2330$ , not usable well.

7th

J. M. Eder.

The spark spectrum of the Nickel and Kobalt behaves similarly (Plate III, FIGS. 9 and 10); in the case of these two metals, the linear band extends further towards the more breakable end and in particular

the nickel spectrum only loses its light power at  $\lambda < 2150$ . That's why I recommend this

Easy to obtain "pure nickel" from the trade (in wire form) as a light source (in the spark spectrum)

to study absorption phenomena more than iron.

It should also be mentioned that the spark spectrum of the Wolfram is similar to that of the Fe, Ni and Co, is very rich in lines; but it does not have an essentially more favorable distribution of the lines;

it does not extend further into the ultraviolet than the spectra of Ni and Co; on the other hand, tungsten has the

Disadvantage that the energy of its spark spectrum is lower than that of Fe, Ni or Co and

one incidentally has to last  $1\frac{1}{4}$  times longer than with these metals.

Occasionally I also used the spark spectrum of the Aluminium or Silicon with success Lead spectra; they are shown in Plate III, Figs. 12 and 13 1). It also seemed

important to me, including the ultraviolet spectra

1. of burning magnesium
2. Drummond's magnesia and zircon light
3. Electric arc light

to be included in these comparative experiments, since they are used as light sources of great brightness in the ultraviolet

are known; the comparison of the spectrum photographs of these three light sources with one another

is made possible by Plate III, FIGS. 6 to 10; For a better overview, the spectrum of the Sunlight (made with the same quartz spectrograph) shown on the same panel. The spectra on this panel were obtained using ordinary silver bromide gelatine plates (without a color sensitizer).

photographed, with the exception of Spectra 9 and 10, which were produced with erythrosine plates,

how to perceive at the sensitization maximum at the less frangible end.

The solar spectrum shown (Plate III, Fig. 2) was photographed above ground on a clear September

and it extended to the Fraunhofer line S (after Cornu). For the purposes In another series of experiments, I photographed the absorption spectrum on the same plate

a 1 cm thick plane-parallel crown glass plate (see Plate III, Fig. 4), as well as its absorption spectrum

an equally thick uranium glass plate (Plate III, Fig. 5), with the same exposure times, of course

(2 seconds) had been observed. For such absorption experiments in the ultraviolet, this is

Well usable sunlight; to study the absorption phenomena of certain other types of glass

(for example the phosphate glasses), however, the sunlight is too poor in more breakable ultraviolet

Rays.

The spectrum of the burning magnesium extends further against with sufficient exposure

the more breakable end of the ultraviolet than is the case with the solar spectrum, as is the case with our weather conditions

is usually available, is the case. The spectrum shown in Plate III, Fig. 6 the burning

magnesium was exposed to light for 3 minutes (slit opening 0.02 mm)

obtained and for comparison a weak spark spectrum of magnesium metal photographed next to it

(Plate III, Fig. 7). It follows from this that the burning magnesium is a almost continuous one

Spectrum delivers, which is with sufficient brightness over the whole visible and ultraviolet

Partly extends to about  $\lambda = 2800$ . From then on the brightness of the more breakable rays is only one

low and the spectrum band stretches relatively slowly even with long exposure towards the more breakable end of the spectrum. This spectrum shows some characteristic magnitudes

1) D & A \ 1, uranium spectrum in Plate III, Fig. 121 is contaminated with iron in it.

About the usability of the spark spectra of different metals.

sium oxide bands, as well as Mg metal lines, which especially Liveing and Dewar 1) exactly

have described. In particular, the strongly inverted and broadened magnesium line falls  $\lambda = 2851$

on; the same line occurs in the magnesium spark spectrum and is clearly visible in Plate III, Fig. 8.

Furthermore, the Mg triplets are in green ( $\lambda = 5183, 5172$  and  $5167$ ), as well as those when burning

Magnesium in the air characteristically occurring magnesium oxide bands clearly recognizable 2), which,

(according to Liveing and Dewar) the wavelength

Magnesia  $\lambda = 5000$

MgO  $\lambda = 4957$

MgO  $\lambda = 4990$

MgO  $\lambda = 4948$

, cc-1

Mg 4980  
O

Mg 4974  
O

Mg 4969  
O

comes to. The burning magnesium would be by virtue of its fairly continuous spectrum of emissions

as a light source for absorption experiments for the spectral region). > 2800 usable, if not the magnesium oxide

Smoke extremely annoying and the restless burning of the magnesium flame extremely annoying would; For examinations in the more fragile ultraviolet, the burning magnesium leaves us in the sting.

It seemed to me that the brightness distribution of this light source was compared with the spectrum

of the magnesia oxyhydrogen light of interest and I brought a pencil of magnesia to

For this purpose a blower (oxygen-luminous gas 3) is used for the scalding; this

Light had approximately the same optical brightness as the burning magnesium ribbon (namely approx

80 candles). The relative brightness was shown when the photograph was taken in a quartz spectrograph

the magnesia oxyhydrogen light in red, yellow, green and blue is greater than in magnesium light;

on the other hand, the intensity of the more breakable rays decreased more rapidly with Drummond's light;

the exposure time had to be taken about four times longer to get a clear ultraviolet

Spectrum in the more breakable spectral regions and despite this longer exposure time

the effect extends less far into the ultraviolet. Drummond's Kalk-und behaves similarly

Zircon light. All of these light sources produced by means of the oxygen-illuminating gas blower only give

in the beginning of the ultraviolet, that's incidental to). = 3500 a sufficient brightness, as also Plate III,

Fig. 8 clearly shows. The spectra of Drummond's light are continuous, with the exception of the

occurring main lines of the burning oxyhydrogen gas (see Volume H2 Oct. and H2 Oß in Plate III, Fig. 8),

as well as the Swan spectrum (especially the C band ~). Furthermore, one notices individual metal lines,

for example the magnesium line). = 2851. Since the intensity of the magnesia oxyhydrogen light at the

specified exposure time is only up to approximately  $\lambda = 3600$  and from), = 3600 to approximately 3500

sinks noticeably, it follows that this light source can only be successfully used for absorption experiments

can use visible spectrum up to region  $\lambda = 3500$ ; the exposure time is extended by

to be able to photograph further areas of the ultraviolet, so arise in the less frangible

Spectral areas often disruptive phenomena of over-exposure (halos, irradiation phenomena, Solarization).

The light of the sun is more favorable for experiments with absorption in the ultraviolet than the drummond's light

Light, since you can count on it to average the solar spectrum when the sun is clear enough of the quartz spectrograph up to the Fraunhofer line S<sub>2</sub> (after Cornu), = 3099

\* 5)

to be able to. Of course, the brightness of the solar spectrum is as a rule no longer significant from R onwards.

1) Kayser: "Spectral analysis", 1883, p. 293.

2) The bands are very clear on the original negatives; the photogravure shows them blurred.

3) The luminous gas flowed out of a gas pipe under the usual pressure, the oxygen at a pressure from 15 to 20 cm of mercury.

7 \*

J. M. Edler.

Neither sunlight extends far enough into the more breakable regions of the ultraviolet, nor the magnesium or drummond's light, but you have to go to the spark spectrum (by means of a powerful Harknifian inductor). Not as far as the latter, but wider than the first-mentioned light sources, the light of the electric Farman arcs is sufficient.

An arc lamp with a brightness of about 3000 candles was available to me (direct current) which was kindly provided by Siemens for my experiments. The arc light was brought into the spectrograph under the most favorable brightness conditions and a spectrum image was produced with an exposure time of 5 seconds to 3 minutes. The shorter exposure

gave a well-defined photograph of the line-rich carbon bands (cyan group #2, 3, and 4 after Kayser); with the prolonged exposure the continuous spectrum occurs up to  $\lambda = 2530$  and

above it more and more strongly, in that at the same time many iron, calcium lines etc. become visible, of which

some are indicated in Plate III, Fig. 10. The most conspicuous (possibly for orientation in the spectrum) line groups

in the spectrum of the electric coal flame arc are:

Cyan band No. 2 (after Kayser). with  $\lambda = 42164197$

4181

4167

Cyan band No. 3 (after Kayser). with  $\lambda = 38843872$

3862

3855

Cyan band No. 4 (after Kayser). with  $\lambda = 35903586$   
3584

then numerous iron lines, including Fe  $\lambda = 3099$  (coinciding with the Fraunhofer Line S<sub>2</sub> in the solar spectrum [Coulson]), furthermore the intensive group of lines

Fe.  $\lambda = 2527$   
2508  
2478.

From then on the spectrum of the electric arc light becomes poor in light.

Finally I mention the spark spectrum of the Kohler, which I skip over of the induction spark between carbon pins (cut from the same carbon with which the Siemens see Arc lamp is provided). This resulted in the characteristic coal lines, which in their entirety do not agree with the arc spectrum, to which Hartley in particular and Adeney<sup>1)</sup> draw attention. Most of all the lines come here

Cyan # 2.  $\lambda$  see above<sup>3)</sup>.

"" "

"" 4. ""

into consideration, furthermore

1) philosopher. Transact. Royal Soc., 1884.

About the usability of the spark spectra of different metals. C $\lambda$  -  $\lambda = 38371$

3836 J.

C 2511

C 2508

C 2478

C 2297

which Hartley and Adeney (op. cit.) occasionally add to the description of the spark spectrum from

Graphite indicated as characteristic lines of the coal spark spectrum<sup>1)</sup>.

These more important carbon lines of the spark spectrum are photographed in Plate III, Fig. 11 reproduced and inscribed the wavelengths; there are also lines of air, iron and calcium etc., which the latter are due to impurities in the coal.

The spark spectrum of the coal can, owing to its more unfavorable distribution of its main lines

do not replace the comparison spectrum I used for an alloy of cadmium + zinc + lead,



which is why I use the latter, possibly using other metal spectra mentioned above than I used the comparative spectrum for my further studies in the ultraviolet, and partly the electric

Arc light (especially for absorption experiments in the given spectral regions) is also used Application brought.

When determining the wavelength of an unknown line which is between two lines of known wavelength, I used simple interpolation as soon as the difference between the wavelengths of the guidelines, for example, was no greater than 30 to 35 Angstrom units. If, on the other hand, the Interval was greater, I calculated using the following formula (from Watts: "Index of Spectra", p. X):

$n_3 - n_1$

$), \sim = \frac{\dots}{\dots}$

$\frac{n_2 - n_1}{n_3 - n_2} = \frac{\lambda - \lambda_1}{\lambda_3 - \lambda_1}$   
 $\lambda = \lambda_1 + \frac{(n_2 - n_1)(\lambda_3 - \lambda_1)}{n_3 - n_2}$

where  $n_3$  and  $n_1$  are the scale parts of the measuring apparatus of the two known lines,  $\lambda_3$  and  $\lambda_1$  the same are corresponding wavelengths;  $n_2$  is the scale number for the line to be measured and  $\lambda$  the one to be determined associated wavelength.

To measure the wavelength of the lines in my spectrum photographs, I have used until now the Hartley-Adeney spark spectra; the aforementioned spectroscopists studied a large one

Number of spark spectra very accurate and gave very precise tables of the wavelengths more numerous

Elements. The Hartley-Adeney numbers are based on the Angstrom-Cornu normal numbers on, as well as on the Thalen'schen wavelengths.

In view of the fact that in more recent times Kayser and Runge, Ames et al Rowland's normal numbers of wavelengths are based on their spectroscopic observations the comparison of both numerical values appears desirable. The following, given by Watts Table 2) enables this conversion for lines from  $\lambda > 2160$  with sufficient accuracy.

- 1) The wavelengths of these carbon lines are given in Hartley-Adeney's treatise.
- 2) Report, Brit. Assoc. Advancement of Science, London 1887, p. 224.

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J. M. Eder.

Correction table to reduce the Angström and Cornu numbers Rowland's wavelengths.

The Hartley-Adeney numbers can be, as far as wavelengths > 3700 are concerned, with sufficient accuracy by means of the above correction table to the length of the Convert Rowland to d'schen normal spectrums or to Kayser-Runge numbers.

For wavelengths < 3700, Hartley-Adeney can be used for a approximate correction Numbers in the following table, which is to a certain extent a supplement to the above table, serve:

Correction table for the reduction of Hartley-Adeney numbers to Rowland numbers Wavelengths.

The relationships between the Hartley-Adeney and the wavelength results more precisely of my reference spectra and the Kayser-Runge's Tellenlängen (which are very similar to Rowland's Numbers approximate) from the following table; this part represents the main lines of mine Usually used spark spectrum of the alloy of cadmium + zinc + lead together associated wavelengths on the one hand according to Hartley-Adeney (partly following Angstrom

About the usability of the spark spectra of different metals.

and Cornu), on the other hand according to Kayser and Runge and according to our own measurements (followed by an Rowland). In addition to Cd + Zn + Pb, this table also contains the spark spectra of magnesium, Thallium and some important Aluminium lines, because these metal lines make im

Reference spectrum sometimes very good services. At the same time the intensity of the lines is the spark spectrum given by (analogous to Watt's "Index of Spectra") the intensity of the brightest line  $i = 10$ , the weakest  $z = 1$  was set.

i metal  
Wavelengths i  
metal  
Wavelengths  
Hartley based on and  
Adeney's) Rowland  
Hartley related to and  
Adeney Rowland

- 1) From then on the Hartley-Adeney numbers are too imprecise and should therefore only Kayser-Runge numerical values are used.
  - 2) Arc spectrum according to Kayser and Runge.
- \*) The lines marked with \* were later by Eder and Valenta with a large Rowland's concave lattice precisely determined and subsequently inserted into the table; they own the same value as the numbers from Kayser and Runge.

About some new lines in the most breakable, ultraviolet Emission spectrum of metallic calcium.

Of

J. M. Eder and E. Valenta.  
Advertisement of the Imperial Academy of Sciences in Vienna, 1893, No. 25.

The real member Mr. Hofrath Prof. V. v. Lang presented the following communication from the gentlemen

Director Dr. J. M. Eder and E. Valenta in Vienna on some new lines in the most breakable, ultraviolet emission spectrum of metallic calcium:

Occasionally an investigation into the emission spectrum of the Calcium in various Temperatures we found a hitherto unknown group of lines in the extreme ultraviolet, which had a shorter wavelength than the most breakable up to now by Kayser and Runge in the arc spectrum of calcium observed (Ca line), = 2200 Å. These lines appeared in the strong induction spark clearly and have the following wavelengths and relative brightnesses (the brightest calcium line  $i = 10$ , the weakest  $i = 1$ ).

Ca line Eder -Valenta Kayser-Runge =  
 2276 Å 03 2275 Å 6  
 2259 Å 5  
 Main line 2208 Å 4  
 2200 Å 1 2200 Å 8  
 Main line 2197 Å 3  
 2170 Å 0  
 2152 Å 3

Ca-Line Eder -Valenta Kayser -Runge 2140  
 3 Å  
 2133 Å 0  
 2131 Å 2  
 2123 Å 0  
 Main line 2112 Å 3  
 Main line 2103 Å 2 2

The wavelengths of other calcium lines newly found in the spark spectrum together with the heliographic ones

Reproduction of the relevant spectral photographs produced by means of the quartz spectrograph

will be communicated later.

Over the line spectrum of elemental carbon in the induction spark and via the ultraviolet spark spectrum wet and dry charcoal.

Of

J. M. Eder and E. Valenta.

(Presented at the meeting of the Imperial Academy of Sciences on January 19, 1893.)

Carbon has two emission spectra, from ... Calibrate the one that S v v see Spectrum, is a band spectrum that occurs particularly when hydrocarbons burn at the Air occurs while the actual line spectrum of elemental carbon passes through the induction spark arises between carbon electrodes.

The Swan's spectrum, whose affiliation to the elementary coal is not undisputed, became already discussed in its full extent into the ultraviolet in an earlier treatise and reproduced heliographically 1). This band spectrum of the coal is now better known. Fewer The line spectrum of coal in the induction base is known. The line spectrum of the elementary K oh 1e n s toffes 2) appears interesting not only because it is the true spark spectrum of the

Carbon between carbon electrodes, but because of its exact knowledge for further Spectroscopic studies of the spectra of the metal salts, which are produced by means of carbon electrodes in the induction spark vaporized is required. It is . namely in all such spectroscopic experiments the elimination of the elementary spectrum of coal is essential.

The line spectrum of the carbon, as it occurs in the induction spark between carbon electrodes, has neither in its general line structure nor with regard to the length of the characteristic lines Lines et 1 v as in common with the Swan spectrum. It became this line spectrum of the coal especially described by Angström and Thalen, who describe the wavelengths of the main lines in the visible

Parts precisely defined and depicted in a good drawing 3). They received the same means a powerful induction spark between graphite electrodes, preferably in a hydrogen atmosphere, to prevent the occurrence of carbon dioxide and carbonic acid. But also in an atmosphere of Carbon dioxide or carbonic acid is what is produced Line spectrum of coal, if one has a strong juductorium with long wire wrapping and Ley den er bottles.

1) cf. page 1 of these treatises.

2) We choose this designation according to K a y s er: "Spectral analysis", 1883, p. 246.

a) Angström and Thalen: "Recherches sur les specters des metalloïdes", 1875 (NoY. Acta Reg. Soc. Ups., Ser. III).

About the emission spectrum of carbon.

In the case of small spark lengths, bands of the Swanian spectrum appear, especially the line groups

in Roth, something that Angström and Thalen already drew attention to.

These two authors

examined only the visible part, as did Watts, whose spectra, however, had many strange lines,

in particular, oxygen lines (according to Schuster) should contain. Both Angström and Thalen, as

Watts give exact wavelengths of the lines observed by them. Ciamician's studies on that Carbon spectrum 1) do not give any more precise information, since there is no determination of the wavelength and

even the theoretical conclusions Ciamician's only apply to the superficial appearance of a small one

Spectral districts are based; moreover was the much wider ultraviolet region of the carbon spectrum

Ciamician unknown. Incidentally, he also drew attention to the fact that depending on the range of the Holtz machine he used, different spectra in Geissler tubes (diluted carbon dioxide) can be obtained. The same is shown after Ciamician

to different spectra, depending on how the light is heard in the narrowed part of the tube or that of the flared ends. When the buttons of the machine with a small one

the er-bottle are connected, so the green light in the capillary tube gives only the carbon oxide spectrum

with buttons very close to the machine; if the buttons are further apart, so begins next to the carbon oxide spectrum the band spectrum (Swan) and the line spectrum of the elemental carbon to occur; if the buttons are still further away, oxygen lines appear on. The light in the enlarged part of Geissler's tube always gives off the carbon-oxide spectrum

(Meeting reports of the Imperial Academy of Sciences in Viena, Vol. LXXXII, 2nd Abth., July issue).

Contrary to these observations, Ch. Fievez 2) opposed the existence of the line spectrum of coal

(Funkenspectrum) at all in question. Ch. Fievez means that that occurs in the spark spectrum of coal

red double line (Fievez and Thalen) at Fraunhofer 'see line C, as well as the light line in orange and many green lines not the carbon, but only the impurities

are attributable to coal. He states that he does too. when using aluminum electrodes

all other things being equal, an orange-red double line in the air in exactly the same way received, only the red double line had merged with the Fraunhofer line

C coinciding line is reduced, which accordingly ascribes Fievez to hydrogen. In a wet substance atmosphere

should only be the only hydrogen line H<sub>α</sub> (Fraunhofer'sche

Line C) remain, on the other hand it disappears in dry air. Fievez's statement is incorrect

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with those of Angström and Thalen, who saw the red carbon line), 16577.5; further

did they not only see the red line of coal between carbon electrodes in the stream of oxygen, but have also observed the same in the luminous gas between aluminum electrodes, namely in the latter

Fall next to the hydrogen line H<sub>x</sub> (Fraunhofer line C), = 6562 · 1 according to Angstrom), while the coal double line with its wavelength with t 1 er (which fear r ö m and Th a 1 e n = - = 6580 indicate) was visible separately. To be sure, the red lines of coal are much less light than the red ones

Hydrogen line H<sub>x</sub> and can therefore easily be overlooked next to this. Indeed they are absent not only with Fievez, but also with Ciamician (a. a. O.) and we also keep their affiliation to the real coal lines for doubtful. We keep the green lines in line with Angs

t r ö m and Th a 1 e n, as well as Ci a m i c i a n, definitely for coal lines and we can each other do not follow the remarks of F i e v e z. The line spectrum of the coal in the induction spark is so weak in the visible part and so uncharacteristic that it does not surprise us takes when F i e v e z overlooked lines, as was the case before F i e v e z with Bunsen (see later);

1) Meeting area d. kais. acad. d. Science in Vienna, 1880, Vol. LXXXII, 2nd Abth., July issue.

") Supplement to the Anna l. f. Phys. U. Chem., 1888, p. 102.

J. M. Eder and E. Valenta.

we have the line spectrum on the other hand, just like Watts, Angs t r ö m and Th a 1 e n, Ci a m i c i a n,

vvah if we arrive at other results as to the number of true carbon lines, when these spectroscopists came.

There is no doubt that the violet lines as well as the ultraviolet lines belong to carbon, how then in general the truly characteristic lines in the line spectrum of coal (spark spectrum) occur in the ultraviolet.

We owe our knowledge of the main lines of the ultraviolet spark spectrum of graphite (Living and Dewar 1), as well as Hartley and Adeney 2), showing the lines of graphitic carbon between), = 3920 to 2297 determined; foreign spectral lines originate in the graphite spectrum from magnesium and especially from silicon, which lines recognized by Hartley and Adeney

and were first eliminated from the coal spectrum. The spark spectrum, on the other hand, is little known

the pure wood kohl; it is such a poor conductor of heat and electricity that electrodes

For these reasons, ordinary charcoal cannot be used to generate an induction spark but must be subjected to a suitable treatment beforehand (see later) Bunsen deals with the emission spectrum of charcoal, occasionally with his

«Spectralanalytische

Investigations »3); he soaked previously made conductive and purified by a violent glow

Carbon electrodes with metal salts, let the induction spark penetrate and thereby obtained the

Spark spectra of various metals. Bunsen says about the spark spectrum of wet and dry

Little coal. In other places he merely mentions: "The dry ones or those moistened with hydrochloric acid

Coal tips of the spark apparatus do not give, if their cleaning has been carried out correctly, no

Spark spectrum, which can be easily deduced from being in an atmosphere of hydrogen

the sparks leaping between them are just the few characteristic lines of hydrogen

give. The sparks jumping over during spectral observations in the air therefore only show air lines of the

Oxygen, nitrogen and hydrogen.

Since Bunsen examined the spectrum of hydrogen only in the visible part, and the spectra,

especially the moist coal, in this district only show faint and very faint lines,

which lie in the less bright blue and violet, they escaped the aforementioned researcher.

On the other hand, we observed highly characteristic and in part very complex spectra

in the ultraviolet, however, which at first seems difficult to disentangle with careful

Experimental setup is easily possible. It will appear in the spark between carbon electrodes, as the case may be

the coal · in the air, in hydrogen or in carbonic acid, as well as in dry or wet

Conditions (in the induction spark) checked spectrographically (quartz), spectra of completely different types

see. The spectra that appear after our experiments are namely:

1. The spectrum (line spectrum) of elemental carbon.

2. The band spectrum of coal (Swanian spectrum), which soon becomes whole, soon again

appears only in fragments, sometimes disappears completely. It occurs especially in the aureole in the

Carbon sparks in a hydrogen atmosphere when weak sparks are used.

3. Cyan bands, in the presence of nitrogen (especially in dry air with strong sparks).

4. Possibly so-called "air lines" in the presence of air, especially with dry coal and strong spark.
5. Possibly the band spectrum of the nitrogen at the positive pole, especially with wet coal and weak induction sparks without Leyser bottles, of course in the presence of nitrogen.
- 1) Liveing and Dewar, Proceed. Royal Soc., Vol. XXX, 1880, p. 152, 494; Vol. XXXIII, 1882, p. 403; Vol. XXXI \ 1882, p. 123. -Philosopher. Transact., Vol. CXLVII, 1882, pag. 187.
- 2) Hartley and Adey, philosopher. Transact. of the Royal Soc., London 1884.
- 3) Poggendorff, Anna!. d. Physics and Chemistry, Vol. V, 1875, p. 369.

About the emission spectrum of carbon.

6. Possibly the spectrum of the water vapor, sometimes mixed with hydrogen and oxygen lines (with moist coal and strong bottle spark).
7. Possibly carbon oxide bands, which are here and there in the aureole of the carbon spark show in the presence of oxygen or carbonic acid.
8. Oxygen lines which, when there is a strong spark, are not only in air, but also in the presence show of carbonic acid.
9. The emission spectrum of ammonia (with wet carbon electrodes, weak induction spark without Leydener bottle and in the air).
10. The absorption spectrum of subnitric acid occurs in closed vessels in the presence of air on (especially in the strong bottle spark). One has to reckon with all these spectra, which are very rich in lines in the ultraviolet, if one generates spark spectra between carbon electrodes and these possibly Fig. 16.

for the study of emission spectra of the metal salts etc., with which the Carbon electrodes soak, want to use.

For a more precise evaluation of these not unimportant spectral phenomena, we make the following experiments.

Manufacture of the electrodes.

\, Vir used charcoal pencils for our investigations, which after using the method specified by Bunsen 1), thorough cleaning beforehand had been subjected.

We waived the use of graphite electrodes in advance and mainly for the reason that a cleaning, like the same with Tips made of amorphous carbon are possible, but graphite does not appear to be feasible and also because graphite electrodes are much heavier when needed Impregnate with salt solutions than the porous charcoal 2).

The charcoal we used was pure linden charcoal (drawing charcoal), how it is put on the market in thin sticks.



The approximately 10 cm long, 6 to 7 mm thick rods were used to make them To make conductive, packed in a porcelain crucible with carbon powder, this one placed in a larger Hessian crucible and the gaps with it again Filled in carbon powder.

The lid was then autlutated with chamotte pulp and placed in the Perr ot'schen gas oven for 12 hours

exposed to the white embers.

After this treatment, the carbon sticks turned out to be strongly sintered, they were harder and

sounding and conduct electricity very well.

These sticks were now cut with a fine steel saw and the small ones from them

The tips produced are 2 to 3 cm long and about 4 mm thick and are successive for several hours

Treatment with hydrofluoric acid, sulfuric acid and hydrochloric acid at theboiling point of the acids in question

underwent ~ m. Between each operation, the fabrics were carefully washed withdistilled water

1) Poggen d o r ff, Anna !. d. Physics and Chemistry, Vol. V, 1875, p. 369.

•) Hart l e y described a method for the production of photographic spectra of the elements by means of salt solutions, by grasping fine graphite threads in a brush-like manner in a glass tube (Fig. 16), the salt solution through the glass tube to the surface kick and let the spark jump (Philosopher. Transact. of the Royal Soc., 1884). This method did not provide us with anything like that favorable results than those obtained using charcoal.

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washed and the same after boiling, then dried and in a well-sealed Vessels kept for further use1).

The arrangement of the apparatus for the generation of spark spectra in the air was already in described in an earlier treatise 2). However, in order to skip the spark also in different gases we have constructed the small apparatus described below, which has proven itself very well in our experiments. The apparatus is shown in the following sketches (Figures 17, 18 and 19). The cylindrical glass body (a) with a volume of approx. 50 cm<sup>3</sup> is perpendicular to the

Axes of length, with their axes

17, 18 lying in one plane, FIG. 20. two longer glass tubes (b and c) and the two short tubes (i and i') melted.

The pipes (i and i ') are used for recording of the electrodes (l' and k '). If these are short, on one end of sealed glass tubes, which exactly fitted Platinum sleeves (p and

: f

p ') included; these latter sin <l with the platinum lugs (l and l ') through into the glass tube melted platinum

----- Cl -----

wires connected.  
The charcoal pins (round r')

a, b, c, d lead wires; e are quartz Plated into the platinum sleeves;  
f drainpipe; g gas discharge;  
h dropping funnel; i electrodes. stuck

and for the sake of easier

Absorption and distribution of the dripping liquids are provided with longitudinal grooves. The approach (b) is a 4 cm long, 8 mm in the clear strong glass tube, which is provided with a ground flange (d) at the free end. To this

the latter is an airtight plate made of mountain crystal cut perpendicular to the optical axis Fig. 19. ground up.

The glass tube m is used for the gas supply, the tube c for the discharge.  
The vitreous

(a) also has a bottle neck in the upper part, in which a rubber stopper is used the two tap dropping funnels (l' and l' ') are inserted in such a way that they allow

-to drip any liquid on the coal tips without letting air into the apparatus penetrates.

The small apparatus, which in the above form is the result of numerous experiments has proven itself in our tests and has served us well. Be low volume allows easy and complete displacement of the air through

the gas in question and its mounting on the spark generator can easily be carried out, as FIG. 20 shows.

With this arrangement, the comparison spectrum can be used with one and the same spark generator without

Disturbance Establish what appears to be of value to the equipment set-up.

1) The cleaning of the charcoal tips was carried out in the laboratory of Prof. Dr. J. O s he at the k. k. technical

University carried out with the greatest care, for which we would like to express our thanks to the aforementioned professor.

2) cf. page 1 of these treatises.

About the emission spectrum of carbon.

The described mounting of the carbon electrodes in platinum sleeves in the apparatus is an advantageous one,

by using simple aids (platinum wire, sheet metal and thin-walled glass tubes) can easily produce a larger number of such electrode holders, which means that they can be replaced immediately is made possible.

Moistening the coal tips with water or with various solutions is quick and easy

can be safely carried out during the operation of the inductor, and the apparatus permits the filling funnel

are closed, with acids or corrosive liquids, their application with free electrodes of the

Spectral apparatus is not feasible to work because of. In that case all that is necessary is the withdrawing ones

To bind vapors or to direct them into the chimney, which eliminates any nuisance from them.

If the electrode carbon is sufficiently thick, as stated, then spectra can be made with strongly moistened

Produce coals using even a very powerful spark from a bottle, thin carbon sticks

would be smashed in the process. Our experimental set-up is suitable in this direction

better than the fulgurators from Delachanel and Mermet<sup>1)</sup> or from Lecocq<sup>2)</sup> or similar

Apparatus 3) in which the experiment only uses weaker induction sparks without L e y den er bottles

can be carried out, as strong bottle sparks throw the liquid in all directions, making observation very difficult.

Despite the most careful cleaning of the coal in the manner indicated, it turned out that

sometimes with very long exposure times the carbon spectrum with a few silicon lines and calcium lines

was contaminated (these contaminants probably originate from the washing machine

Kohlens: itzen used distilled water), of the alkali metals only Na (namely the yellow Line).

The elimination of these lines is easy on the one hand by comparing the wavelengths of the relevant lines

Lines; we have especially the line spectrum of silicon in another treatise

described for this case 4). To increase the security of the relevant determined spectrum lines

, v were comparative spectra of calcium metal, silicon, magnesium and aluminum over the carbon spectrum

photographed and in this way. controls the results of the calculation.

In the experiments on the coal-spark spectra in various gases, one must carefully pay attention to the

The ability of coal to absorb gases must be taken into account. If you are with the same Carbon electrodes would work one after the other in different gas atmospheres, it was easy to sit down

the danger of making mistakes, which one avoids by using the type of gas to hit the coal tips changes, possibly this in the \_gaseous atmosphere in which you want to use it, beforehand anneals.

In the following those emission spectra shall be described, which in the induction spark between electrodes of amorphous carbon arise under different conditions:

1. Spark spectrum between carbon electrodes in dry hydrogen or Carbonic atmosphere.

1. When the induction current of a powerful inductorium between carbon electrodes in a An atmosphere of pure, dry hydrogen overturns, so arises at ordinary atmospheric pressure a bright spark of the familiar reddish-violet color caused by hydrogen. Man receives a well-defined photographic spectrum depending on the exposure time of 5 to 20 minutes,

1) "Compt. rend. », Vol. LXXXI, 1878, pag, 726,

1) Lecocq de Boisbaudran: "Specters lumineux" 1874.

1) S. S al et: "Traite elementaire de Spectroscopie", 1888, p. 157.

•) Comp. p. 75 of these treatises.

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in which the lines appearing on a weakly lightened ground 1) appear very clearly. Next the coal lines occur hydrogen lines, namely

Mr., J = 6562 (Roth)

Hß, i, = 4861 (green) Hy,)

.. = 4340 (blue)

H \) .. = 4101 (indigo)

· Of which the lines H [': >, Hy and Hö are enormously broadened and in spectrum photography as broad bands, which are gradually shaded from the middle to both sides, appear. The other hydrogen lines of smaller wavelengths either do not come to the Appearance or emerge only very weakly (in the case of greatly prolonged exposure) 2).

In the heliographic illustration (Plate IV, Fig. 7) the above-mentioned broadened hydrogen lines are shown clearly. The actual carbon lines (Lini enspectrum of amorphous coal) appear very clearly under these conditions. As for the visible spectrum, studied we do the same in an atmosphere of dry, pure hydrogen and one of luminous gas by means of a Krüss spectral apparatus.

We did not notice any characteristic line in the visible spectrum, so it was as if it seems understandable that Fievez is destroying the whole visible spectrum of lines of carbon. attributed to the purifying secondary constituents of the carbon electrodes used in the experiments. vVir  
f 6583 I

neither did Fievez see the Angstrom-Thalenian red double line of), = 16,577.  
5 y

clearly, only when changing the current of the inductorium reinforced with bottles we could at strong approached coal tips a faint flash at those points where the lines are supposed to be, to confirm. In view of Angstrom-Thalen's careful observations, we have but these red carbon lines have not been deleted, but only described as doubtful. On the other hand we could from the yellow Angstrom-Thalen line group of

) .. = 5694 · 1  
 ) .. = 5660 9  
 ), = 5646 x 5  
 ) .. = 5638 6

in spite of the most careful search of the spectral region in question, neither in the hydrogen nor in the  
 Notice any hint of coal gas atmosphere, which is why we take no decency, this To delete lines from the register of true carbon lines.

We saw the yellow-green Angstrom-Thalen coal line) = 5379 · 0 in our coalr5150 5, clear, albeit weak, also the triple green line), = 15144 · 2 JI, which goes into one of the

5133 · 0

Swan's band is embedded; we did not succeed in resolving it as clearly as the same angstrom and Thalen seem to have succeeded, but according to our observation we rank this group of lines

1) The continuous spectrum is brightest at the beginning of the Utiaviolet and assumes around A ~, rno o 'i'asch Intensity. It probably comes from the carbon electrodes that were on the extreme tip during the experiment become brightly glowing.  
 ") All · this information applies to normal air pressure.

About the emission spectrum of carbon.

the spectrum of pure coal. The purple Angstrom-Thalen line is quite unquestionable  
 $\lambda = 4266 \times 10^{-8}$  a true line of the carbon spectrum; however, we found the wavelength a bit longer,  
namely  $4267 \times 10^{-8}$ ; this line can be photographed much more clearly than observed.

\ i \ Tir must therefore explain that, according to our observations, Fievez is decidedly mistaken  
is when he is the whole spectrum of lines established by Watts, as well as by Angstrom and  
Thalen

Attributes coal only to the impurities of the carbon electrodes and the existence of all in this regard  
denies given carbon lines. After what has been said above, we can only choose to delete it  
understand the Angström-Thalen line group (yellow-green)  $\lambda = 5694$  to  $\lambda = 5638$ , but hold  
it

(apart from the doubtful Angstrom-Thalen's red double line) the following in

\ .Inser

Directory of recorded lines of the line spectrum of coal for true carbon lines;

however, they are all relatively weak and not numerous. Of the extremely numerous, of \ V a t's

We were able to find lines ascribed to the line spectrum of the charcoal when using pure charcoal  
and a dry hydrogen or luminous gas atmosphere do not notice anything, so the whole thing

List of Watts' spectrum of lines 1) on the number of Angstrom-Thalens that we have reduced

Coal lines must be reduced. \ Vir use these lines in what follows later Table, namely with  
their \ i \ Tellenlengths, based on the Rowland's normal spectrum.

The powerful action of the coal spectrum begins on brown silver plates in the quartz spectrum  
at  $\lambda = \sim \lambda 4267$  and the most breakable photographable line has a wavelength of  $\lambda = 2296$ .

These lines and their relative energies can be seen from Plate IV, FIGS. 6 and 7; over the \  
Wellenlängen  
same see later.

In addition to the actual line spectrum of the charcoal, there are (especially in the aureole)  
the

Bands of the Swan spectrum, if the spark between carbon electrodes in a \ i \ hydrogen  
or the luminous gas atmosphere flashes over. In particular, it is the main lines of the light  
green band

(Carbon band according to Eder with lines 4736, 4714, 4697, 4684, 4677); it is remarkable  
that the highly characteristic ultraviolet bands of the Swan spectrum in the spark spectrum  
of carbon both in a hydrogen and in a carbonic acid atmosphere entirely absent, at least this is  
always the case when at normal atmospheric pressure and with strong  
Spark is worked.

If the carbon electrodes are surrounded by an atmosphere of dry carbon dioxide, this is how the color of the major appears a striking spark when using Leydener bottles bluish; the brightness is greater than in a hydrogen atmosphere and the photographic efficiency almost twice as large as in the latter case.

The line spectrum of the amorphous coal remains the same as in the hydrogen atmosphere, however all the main lines of the coal spectrum emerge more clearly 2). In addition, make up next to the coal lines numerous strong lines still perceptible, which belong to oxygen; apparently dissociated the carbonic acid at the high temperature of the induction spark reinforced with Leydener bottles, for nothing to be noticed of the appearance of carbon monoxide. Fig. 6, plate IV, shows the picture of the Spark spectrum of amorphous coal in a carbonic acid atmosphere.

The spectrum of oxygen appearing under these circumstances next to the carbon lines appears, especially in the less frangible part ( $\lambda > 3000$ ), very distinct, the strong, close together Lines of oxygen lined up in a row sometimes even make it difficult to find the carbon lines. In the more breakable part, on the other hand, the carbon lines appear all the more clearly.

- 1) S. Kayser: «Spectral analysis»; also Watts: "Index of Spectra".
- 2) Hartley stated, as to the spark spectrum of graphite, that the carbon lines are in a carbonic acid atmosphere become longer, but otherwise remain unchanged.

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Table of the wavelength of those lines that appear in the line spectrum of amorphous coal, occur in both a hydrogen and a carbonic acid atmosphere.

- 1) Liveing and Dewar's «Linienspectrum des Carbones» contain many lines which Hartley as silicon lines recognized; these are to be deleted from the relevant tables (including Kayser's Spectral Analysis, 1883) (cf. Hartley: Philosoph. Transact., 1884 and Watts: "Index of Spectra".
- 2) This cyan line is given by Liveing and Dewar.
- 3) Exner and Haschek give here a coal line,  $\lambda = 3165$ .
- 4) These two lines, 2498 and 2496, should, as Exner and Haschek pointed out, belong to boron (E. and V.).

About the emission spectrum of carbon.

To find the actual carbon lines belonging to the line spectrum of the amorphous coal, the spark spectrum of coal in a hydrogen atmosphere on the one hand and in a Carbonic atmosphere, on the other hand, were photographed among themselves and only those lines were in Considering which two Spectra were common.

Careful measurement of the lines resulted in the wavelengths given in the table on p. 66 (A. E.) for these carbon lines. It should be noted that these wavelengths are based on Rowland's

Normal spectrum and, in the frangible part, were related to Kayser and Runge's numbers.

In this table are the lines we found in the line spectrum of the amorphous coal and the numbers Angstrom and Thalen's, Liveing and Devvar's and Hartley and Ade n e y's<sup>1)</sup> placed next to it for comparison. In addition, we have the starting edges of the characteristic Cyan bands included in the directory, namely the relevant wavelengths with the numbers Kayser and Runge's 2), with the exception of the more breakable cyan band edge),

= 3360, which Liveing and De observed was directed in the cyan, while Kayser and Runge measure the cyan bands that form in the galvanic arc between carbon electrodes occur in atmospheric air.

The comparison of ours in the spark spectrum of coal (both in a \ hydrogen and in a carbonic acid atmosphere) found ultraviolet lines with the starting edges of the so-called

Cyan bands show that a small part of those present in the coal spark spectrum are weaker Lines with the main lines or characteristic starting edges of the cyan bands, Cy No. 3 and No. 4 (numbering according to Kayser and Runge), match, so these are available are. These are the lines:

Coal spark spectrum according to our regulations (A =

3883 8

j 3872 011

3861 6

3854 5

! f 3590 1

l 3585 6

3361 · 0

3

2

Starting edges of the cyan bands according to Kayser and Runge. first edge of

Cy band No. 3). = 3883 x 6

second

""

3 3871 5

third



""

3 3861 9  
fourth 3 3855 · 0  
first  
""

''  
"

4 3590 5  
second  
""  
4 3585 9

Cyan band according to Liveing and De was 3360 · 0

On the other hand, in our experiments we were able to detect the presence of lines of the less breakable

Cyano group (No. 1 and 2) do not notice as soon as we put the carbon spark in a hydrogen or Let the carbon atmosphere skip over and its spectrum with the help of the quartz spectrograph photographed.

This may be due to the fact that cyan bands Nos. 1 and 2 are photographically are relatively less effective than cyan band No. 3, which is by far the brightest, while Cy No. 4 still brighter it is as Cy # 1 and 2, but less bright than Cy # 3. Therefore step at Always photograph a very weak cyan spectrum first on the edges of cyan band No. 3, then only those of Cy No. 4 and, much later, only hints of Cy No. 2. (In the Funkenspectrum

1) S. Watts: "Index of Spectra", 1889, pag. 31. - Hartley and Adeney: "Measurement in the Spectra of elementous substances », philosopher. Transact., 1884.

2) Kayser and Runge: "On the Spectra of the Elements", Abhandl. · D.royal prussia. Akad. D. Wissensch., Berlin 1889, 2nd section: About the band spectra of carbon occurring in the galvanic arc. (The same bands appear in the Cyan.)

J. M. Eder and E. Valenta.

The weak cyan bands No. 1 and 2 also clearly emerge from the charcoal in the air [see later].) The appearance of the cyan bands in the cob spark of course only happens when nitrogen is present.

But even the slightest traces of nitrogen in a hydrogen or carbonic acid atmosphere are quietly betrayed by the appearance of the main cyan lines. By carefully cleaning the charcoal from absorbed air and prolonged washing of the apparatus with pure dry hydrogen you can make the cyan lines recede, but we do this when using a Line spectrum

of the elementary amorphous carbon (spark spectrum). (Based on Rowland's standards.)

il \ 'Vellenlingen il Inten1

! according to Eder and: 1 sity 1 R cm · er k u n g c nl! Valenta ij,: 1

11! I.

~ ---- ~ ~ -, -! [

6584 · 2 II ::! =, ===== · ==

Roth 1 '.\_ · 1 i. ) - questionable whether belongs to carbon \ 6578 · 7 I ·

1

1 yellow green · I 5379 8 I, 5151 ·

2

Green (5144 9

5133 7

· (4556 3V1oletl- (

Main line, widens in the strong bottle spark 4267 · 15 \* 43921 · 38 \* 2

slightly broadened

3877 · 0

3848 · 0

2993 · 2 tverbreitert nebeli0 · 2967 · 6} '"

2905 · 4 very weak

2837 · 84 \* 4

2836 91 \* 1 6 H a u p t l i n i e 1)

2747 3 3

Ultraviolet 2641 · 4

2576 7

2554 6

2512 08 \* 5)

} sharp 2509 16 \* 3

2478 64 \* lo in ten si vste main line 1) 2402 · 1

shadowy

2343 · 5)

2342 6 ~ faint, foggy

2332 · 5 1 y

2296 94 \* 6 widened, main line 1)

\*) The wavelengths marked with an asterisk were later (1899) we used one large concave grating new (with an accuracy of 0x03 -A. E.) determined -and -are instead of inaccurate readings were made by means of the quartz spectrograph (E. and V.).

') 2S36, 24.8 and 2296 are particularly characteristic.

The carbonic acid atmosphere was unsuccessful because the carbonic acid prepared from marble and hydrochloric acid, probably because air bubbles were trapped in the marble always contained traces of nitrogen.

It is noteworthy that Hart l e y and Ade n e y are among the coal lines measured by them also those of the length} = 3881 \* 9, 3870 \* 7, 3589 \* 9, 3584 \* 8, which after above as the starting edges of the cyan bands and from the list of the line spectrum the coal must be canceled. Liveing and Dewar got fed up with their older work the graphite spark spectrum does not record these lines, but these were first identified as "new ones." Hartley and Adeney (op. Cit.) Coal lines established. For the spectroscopist who

has to do with the line spectrum of the carbon, especially in the case of it with impregnated carbon electrodes works, the appearance of the main cyan lines is of interest.

About the emission spectrum of carbon.

\, Much more from the comparison of the wavelengths determined by us for the spark spectrum the amorphous charcoal and that of the graphite can be seen, the same line spectrum comes to both to. According to what has been said, the lines of the elementary carbon spectrum are flat For those given in the table on p. 68, which in all likelihood are due only to carbon belong to include.

With regard to the line spectrum of the elementary carbon, as it is in the spark spectrum between carbon electrodes occurs, it should first be noticed that it was not tied with the lines of the coals identified which occur in the galvanic arc between carbon electrodes; this results directly from the comparison of the characteristic starting edges of the coal bands No. II and III (in the coal flame arc after Kayser and Runge), the wavelengths of which are the following, with the Spark spectrum of elementary carbon (see our table):

A.

, ---, . \_\_\_\_\_  
First edge of C-band No. II in coal flame arc 5635 · 4 Second edge  
5585 5  
Third edge 5540 9  
First edge of C-band # III 5165 x 3 Second  
edge. 5129 · 4  
First edge of C-band No. IV. 4737 · 2 Second  
edge 4715 3  
Third edge 4697 6  
First edge of C-band # V 4381 \* 9  
Second edge 4371 3  
Third edge 4365 \* 0

All of these characteristic lines are absent from the spectrum of lines that we have described elementary carbon, which thus represents the real line spectrum of elemental carbon is to be designated.

II. Spark spectrum between carbon electrodes in atmospheric air.

One brings electrodes made of cleaned and made conductive carbon to the spark generator If the atmospheric air enters and causes the strong induction spark to flash over, this results in:

1. The same spectrum of lines in coal as in a hydrogen or carbonic acid atmosphere (see before).
2. The so-called air spectrum, which emerges very strongly and the inevitable companion the spark spectrum is in analog cases (also with metals). It is clearly visible in Plate IV, Fig. 4

and makes it very difficult to find the coal lines in the less frangible part, one calls it with spectroscopes

of less dispersion works, since the air lines by virtue of their strong photographic quality Effectiveness emerge strongly.

3. In addition to the air spectrum, the cyan bands occur on the.

The cyan band No. 2 appears in the photographic negative, but above all the most intensely developed one

Cyan band No. 3 and then cyan band No. 4.

Plate IV, Fig. 4 gives a clear picture of this phenomenon, which can be seen by means of the quartz spectrograph

with a small gap opening and use of a large inductorium, as well as several Leyden bottles was photographed. The affiliation of the strongly confused line groups to air, cyan and carbon is indicated on this figure.

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The cyan bands appearing in the spark spectrum of the charcoal in the presence of air were

by us for complete identification with those in the galvanic arc (carbon electrodes in the air)

Occurring cyan bands subjected to a precise measurement and showed the sharp edges of the Roth limited, but gradually shaded towards the breakable end and made up of numerous fine lines

consist. In addition to these edges measured by us, the Kaysers-Runs are comparatively similar

The wavelengths of the cyan bands in the galvanic arc are listed in our table, namely the characteristic starting edges of the most intense cyan bands, which even with spectral apparatus from

low dispersion! are easy to find.

Cyan band # 2, first edge 4216

second

"

4197

third 4181

fourth 4167

fifth 4157

Cyan band # 3, first edge 3884

second

"

3872

third 2862

fourth 3855

Cyan band # 4, first edge 3590  
second 3586  
third "  
3584

In Plate IV, Fig. 4, these cyan bands are identified in more detail; the same make themselves very intrusive noticeable, in such a way that they often completely cover other lines which lie in the same districts, when using spectrographs of lower dispersion.

Therefore the presence of air should be avoided as soon as line measurements in the coal spectrum are to be made.

The porosity of the charcoal favors the formation of the cyan bands by the in the pores the coal absorbed nitrogen of the atmospheric air combining with the carbon to cyan has the consequence. The charcoal gives these cyan bands both when there is a strong bottle spark and with a weak induction spark without bottles, while they are much weaker with graphite electrodes occur.

Finally, it should be noted that when carbon electrodes are placed close and weak Sparks in the atmospheric air in the aureole of the spark hints of the spectrum of carbon dioxide finds; they disappear when a strong bottle spark is used. Annoying side effects we observed when the carbon spark spectrum is generated in closed glass vessels filled with air becomes. The spark causes the formation of red vapors of subnitric acid in a very short time, which soon multiply to such an extent that the emission spectrum of the spark is absorbed in the atmosphere filled with red sub-nitric acid vapors.

III. Spark spectrum between carbon electrodes moistened with water in one Atmosphere of hydrogen or carbonic acid.  
Using suitable devices (see above), charcoal is strongly moistened with water and The induction spark produced between such electrodes is produced according to the type of spark

About the emission spectrum of carbon.

several spectra of quite different appearance. \ Vir reproduce four such spectrum photographs in Fig. 8 to 11, Plate IV, namely:

Fig. 8 Wet carbon electrodes in hydrogen spark with 3 bottles"

"

Spark without bottles"

10

""

Carbon dioxide spark with 3 bottles"

11

"Spark without bottles.

The phenomena occurring here can be summarized as follows:

1. Wet charcoal gives with the powerful inductorium reinforced by Leydener bottles in a vacuum a first of all a fairly light red-violet sparks. The widened spectrum Hydrogen lines and all carbon lines also appear after an exposure time of a few minutes as in the case of dry coal in hydrogen. In a completely analogous way, wet coal gives a carbonic acid atmosphere the oxygen and carbon lines. In both cases there are faint hints of the spectrum inherited from the, and in particular the brightest ultraviolet water band 'I .. (designation after Eder), the characteristic borderline of which is at  $\lambda = 3063$ . Contains that to moisten the If carbon electrodes are used, if mineral salts are used, their spectral lines appear very strong, for example  $\text{Ca Cl}_2$ ,  $\text{Si Cl}_4$ ,  $\text{Na Cl}$  etc. 1).
2. An induction spark produced between wet carbon electrodes without a Leydener bottle is less light and bluish in color. In the visible part there are no lines at all other than those which may result from any contaminating metal salts present. After several hours Exposure time, however, we received well-defined spectrum photographs in the ultraviolet. It was found under these circumstances when using wet charcoal in a hydrogen atmosphere above all a strong water vapor spectrum (see Fig. 9), both the water band 'I .., as well as 'I', whose boundary lines lie at  $\lambda = 3063$  and  $2811$  and which are made up of numerous fine lines exist. Even in a carbonic acid atmosphere, the wet charcoal gives without application of Leydener bottles, above all the mentioned water bands and relatively even lighter than in a hydrogen atmosphere (see Fig. 11). The gas spectra recede in both cases and the hydrogen spectrum in one case as well as the oxygen spectrum in the other (carbonic acid atmosphere). The line spectrum of the cohorts itself appears only very weakly and in its strongest main lines on. In particular, the most breakable lines in the spark spectrum of wet coal are without bottles Almost undetectable in a hydrogen atmosphere. The induction spark favors without a bottle thus the formation of the water vapor bands and allows the element spectra to recede, during the

Induction spark intensified the emergence of the element spectra with the help of Leyden bottles favored, so that in the latter case coal and metal spectra emerge more clearly, but in addition also the hydrogen and oxygen lines and a weak water spectrum. The least are disturbing, foreign ultraviolet spectral lines when using clean, wet carbon electrodes and of a strong bottle spark, since in this case only the main lines apart from the carbon of hydrogen (H $\alpha$ , H $\beta$ ; 'i, H $\gamma$ , H $\delta$ ) and weak water bands appear. The genesis strong water bands are often undesirable, since they are very broad and all in their area cover foreign weaker lines.

1) The calcium lines are often more powerful than the carbon lines, even if only traces of calcium salts are present in the Dripping water is present, all other things being equal. Silicon only appears in the main lines and is less obtrusive than calcium. The appearance of calcium lines can possibly be exploited quite well by looking at them Use narrow, sharp lines as guidelines. 72 J. M.

Eder and E. V a l e n t a.

#### IV. Spark spectrum of wet coal in the air.

If the induction spark produced without Leyden bottles is involved Water moistened carbon electrodes in the air over, so arises

1. a strong spectrum of water vapor, namely the 'i \ Tasser bands (/ . And[: i;
2. Furthermore, the line spectrum of the elementary coal emerges (in its main lines);
3. appears the ultraviolet A r n r n o n i a k s p e c t r u m with its characteristic bands' l, ~ and y;
4. the actual well-known air spectrum consisting of numerous lines, which at dry carbon electrodes in the air with strong bottle spark easily emerges, steps back and the nitrogen band appears in its place. This is how the spark spectrum with the wet charcoal in the air has a very peculiar appearance, as can be seen from Fig. 5, Plate IV. The nitrogen band spectrum presented here is the so-called nitrogen band spectrum of the positive pole according to Hasselberg 1), which Angstrom and Thalen ~) probably mistakenly believed to be the spectrum of subnitric acid. It is well known that nitrogen gives two different band spectra, which the glow light (aureole) of the in the air between carbon or Metal electrodes causing spark that are different at the positive and negative poles is. The latter glow light spectrum occurs much weaker than the former. Accurate measurements of this Angstrom and Thalen and Hasselberg gave nitrogen band spectra.

It is remarkable that the Spectrum of glowing light in the open air or in pure nitrogen,

occurs in the Geyser pipes both at normal air pressure and in dilute air. There According to Angstrom and Thalen, especially when the electric spark flashes in the air a lot of subnitric acid forms at the positive pole, they write the bands specific to nitrogen at the positive pole towards nitrogen dioxide. However, this view has been contested and the spectrum in question is today generally ascribed to nitrogen itself<sup>3)</sup>, while one the band spectrum of nitrogen at the negative pole as a second, also elementary nitrogen associated spectrum.

Hasse 1 b erg uses photography to precisely measure the nitrogen spectrum in Geissler's tubes, namely at the positive pole and the negative pole («Memoires de l'academie des sciences de St. Petersbourg », III. series, t. XXXII, No. 15, 1885) without addressing the question to admit closer to the origin of the spectrum at the positive pole; he writes the spectrum to Nitrogen itself too. The starting edges of the breakable nitrogen bands in Geissler's tubes certain Deslandres ("Compt. rend.", 1866, vol. CIII, pag. 375).

For our investigations, this nitrogen band spectrum at the positive pole is a special one Interest, because under certain circumstances it is very clear in the spectrum of the air between carbon electrodes overturning induction spark occurs, on the other hand sometimes completely receding. The Spectrum the wet coal in the air in the induction spark without Leyden bottles, namely, the in the The ultraviolet nitrogen bands contained in the upper table on p. 73.

The starting edges of these nitrogen bands can be measured fairly sharply, but they widen with longer exposure and are not as sharp at atmospheric pressure as in Nitrogen at reduced gas pressure; therefore we only have the lengths of these edges on four digits indicated approximately exactly.

- 1) Watts: "Index of Spectra". -Hasse 1 b erg: Mem. Acad. St. Petersbourg, 1885, No. 15, Vol. XXXII.
- 2) Angström and Thalen: «Recherches sur les specters des metalloïdes», 1875; Upsala Nova Act. Reg. Soc. Sc. Ups., Ser. III.
- 3) cf. Kayser: «Spectralanal., 1. se», 1883, p. 297.

About the emission spectrum of carbon.

5. Incidentally, in the spectrum of wet charcoal in atmospheric air occurs with long exposure and using the induction spark without a Leydener bottle, the ultraviolet band spectrum of ammonia (emission spectrum of ammonia), its occurrence among these Wavelengths



1

the starting edges of the nitrogen bands in the nitrogen band and z,: var  
measured ar. the sharp one, the Intenspectrum  
at the positive pole

Roth facing side in the spark spectrum sity according to Hasse 1 b ergthe wet coal in  
the air and De s landres

4270

4200

4141

1

1

1

4269

4201

4141

1bJJI ~

4058

3997

5

4th

4059

3998

f ~

J: r;

3942 3 3941 5

3803 8 3804 . 2

3755 7 3754 4

3711 1 3709 3

3683 1

3639 1 3640 . 9 "" "" ....

3576

3536

9

7th

3576 . 0

3536 4

'O

". :::

""

3499 2 3499 1 0

3369 10 3370 8

2976 6 2976 1

2962 5 2960 8

2953 4 2952 4

Circumstances was previously unknown and its identity proof by comparison with Ed e r's  
Ammonia bands (y, ö, e, ~) succeeded 1). The ultraviolet ammonia bands are very  
characteristic;

to prove the affiliation of the bands formed in the spectrum of the wet coal in the air  
We measured a few main bands for ammonia in this spectrum. It  
resulted:

Starting edges of the ones in question

Bands in the spark spectrum (without bottle) the wet coal with air admission

Eder -Valenta

), (A. E.)

f2594

2593

2587

l2585

(2478

12477

<24711

~ 2469

Ammonia bands

in the ammonia flame spectrum

after Eder

Ammonia band o), (A. E.) a

2594 7

b 2593 4

C 2586 • 8

d 2585 3

Ammonia band e

a 2478 • 0

b 2476 6

C 2470 • 7

d 2469 5

The remaining bands were not measured any further because their coincidence with the ammonia bands

was clear and the above measurements are sufficient for identification.

1) Eder: cf. p. 32 of these treatises.<sup>10</sup>

J. M. Eder and E. Valenta. About the emission spectrum of carbon. Finally we mention that minor mineral constituents which are directly related to the

Ammonia have nothing to do with the appearance of the ammonia bands in the spark spectrum of the wet

Conspicuously convey coal without bottles; so occurs, for example, when using a calcium chloride solution

or aqueous hydrochloric acid instead of water to moisten the coal, the ammonia spectrum much earlier and more vigorously than if pure water had served to moisten the coal.

About the most favorable conditions for the production of metal spectra Charcoal electrodes impregnated with metal salt solutions.

The comparison of the spectral phenomena in the induction spark between carbon electrodes is particular

Regarding the use of the coal tips for the purposes of testing

Metal salts of concern in the ultraviolet part of the spectrum with the aid of photographic methods.

It turns out that the spectrum of coal in a hydrogen atmosphere, both dry and with wet coal, shows the fewest lines and this arrangement using a strong one Induction spark is most suitable when it comes to the production of metal spectra by means of carbon electrodes,

which have been moistened with the appropriate salt solutions. A good We received proof of the usability of the method on the occasion of the examination of chlorosilicon and silicic hydrofluoric acid, which we published in the treatise "About the Emission spectrum of silicon and the spectrographic evidence of this element

»(see p. 75

of these treatises). Here came the small number of carbon lines in the most breakable Parts of the coal spectrum are very well equipped. The method proves itself for the study of Emission spectra of liquids in the ultraviolet can be carried out easily and safely.

The emission spectrum of elemental silicon and the spectrographic evidence of this element. Of

J. M. Eder and E. Valenta.

(Presented at the meeting of the Imperial Academy of Sciences in Vienna on January 19, 1893.)

The crystallized silicon gives a clear line spectrum when one looks at the induction spark

can break through between such electrodes. The same spectrum occurs when vigorous

Sparks penetrate through an atmosphere of silicon chloride or silicon fluoride. The emissions

spectrum of silicon has been the subject of studies several times. Plücker describes in one

Treatise on "The Constitution of the Electric Spectra of the Various Gases and Vapors" (Poggen

dorff's Annal., 1859, vol. CVII, pag. 531) the spectrum of silicon chloride in Geissler's tubes.

He found (next to hydrogen and chlorine lines) a red stripe belonging to chlorosilicon ( $\text{Si Cl}\beta$  - 'X

of) = 6329, a slightly weaker stripe in the orange ( $\text{Si Cl}\gamma$  - 'X of), = 5978 and one

(5050)

the same green double stripe with a light line in the middle ( $\gamma$ ), = 5036, then two dark ones

violet stripes, the middle of which he was wet, but which were unsafe. Plücker also noted

that bromine silicon in the pipe gave the pure spectrum of bromine.

Troost and Haudouille first described the spectrum of silicon, which they obtained by means of one

Induction spark between electrodes of silicon or platinum in an atmosphere of chlorine

or fluorosilicon flashes received. The same spectrum also occurs between silicon electrodes at the

Air on.

Troost and Haudouille do not give measurements of the wavelengths, but relate them to.

appearing lines on arbitrary scale parts of your spectroscope. According to the above, this contains

Silicon spectrum brilliant lines of all colors with three maxima, one of which is close to the Fraunhofer line

Fraunhofer's line E lies, the second consists of two brilliant lines between green and blue and

the third appeared as a band in indigo blue between 76 and 78 near Fraunhofer's line H («Compt.

rend. », 1872, vol. LXXIII, pag. 620).

Sal et reported that the elementary line spectrum of silicon is found in the spark spectrum of all

Hall's-S! It gives the wavelengths of the characteristic main lines

1) Salet: Theses presentées à la faculté des sciences de Paris "sur les spectres des metalloïdes", Paris 1872. Also

Salet: Annales de Chim. et Phys., 1873, Ser. IV, Vol. XXVIII, p. 65.

10 \*

J. M. Eder and E. Valentini.

(see later) and the drawing of the silicon spectrum reproduced in FIG. Salet also studied that

The spectrum of chlorosilicon, bromosilicon, and fluorosilicon first found by Mitscherlich

more accurate. These connection spectra arise when a mixture of hydrogen is burned with the concerned halogen-silicon vapors; with silicon hydrogen, on the other hand, Salet received no characteristic features

Spectra, as this body disintegrates too easily. Fig. 21.

Main lines of:

1. Hydrogen spectrum (in the visible part) in the Geissler's tubes
2. at normal atmospheric pressure
3. J. Spectrum of chlorine
4. Spectrum of the elementary Si in the spark
5. Flame spectrum of the burning SiCl<sub>4</sub>
6. "SiBr<sub>4</sub>"
7. „ Fluorine and Fluorosilicon

Of the spectra of chlorine and bromine silicon, Salet gives the drawing Fig. 21 and divides it

Wavelengths of the characteristic lines with (see later). Received a similar spectrum of burns Mitscherlich mean fluorosilicon and hydrogen 1).

Ciamician 2) un investigated the line spectrum of silicon with the aid of chlorosilicon and fluorosilicon and an induction spark, as Salet did. It gives, similar to carbon is the case, two spectra for silicon, namely a silicon spectrum first and such a second

Order. The line spectrum of the second order arises according to Ciamician only with the help of strong bottle discharges, preferably using a Hochz machine. With weak discharges

1) Poggendorfs -Anna!. d. Phys. and Chem., 1863, vol. CXXI, pag. 459.

•) Meeting area. d. kais. acad. d. Wissensch., Vienna 1880, Vol. LXXXII, 2nd Abth., Pag. 435.

The emission spectrum of silicon.

the striped bands of the silicon spectrum of the first order also arise (analogous to the Schumann Carbon spectrum, which corresponds to a lower temperature).

The line spectrum of the first order could be completely free of lines of the spectrum of the second order

Ciamician not received. The indication of wavelengths is missing from Ciamician; one is therefore

forced to limit himself to his inadequate photographs and drawings of the Spectra.

Little is known about the ultraviolet spectrum of silicon; some of the main lines

These have been described by Hartley and their wavelengths are also given (see below our table).

The exact investigation of the line spectrum of silicon seemed to us to be of particular importance, as we occasionally examine the spectra of the alkaline earth metals, as well as those of amorphous coal

I encountered many lines, sometimes very strong, showing impurities in the metals mentioned were due to silicon. Since we now have lines as well as the well-known lines of silicon

found in the ultraviolet, which we did not know, but whose origin we found in a content of Suspected alkaline earth metals in silicon, without us knowing about it from the previous information

We subjected the spectrum of silicon to an exact, in-depth study Examination. For this purpose we first put crystals of silicon in sleeves from platinum sheet and left the spark of a large inductorium, reinforced with Leyden bottles

overturn; this happened when air was admitted. The spectrum of the silicon was now determined by means of the

photographed quartz spectrographs already described in an earlier paper. The pre-rehearsals soon showed that our silicon was contaminated with iron and aluminum. We sought now that

Eliminating lines of these elements from the spectrum of silicon, which we also succeeded in that with the help of which we can erase the spark spectrum of the metals mentioned above below that of silicon

Slit bars photographed our orientation spectrum on the other hand

an alloy made of lead, cadmium and zinc, photographed to the wavelengths to be able to measure the silicon lines in question. As it subsequently turned out that

as a result of the very small crystal fragments of silicon used, of which only a small part the platinum setting, the flashing spark sometimes its starting point from the

We feared that platinum lines would appear and took photos

For possible elimination of the same from the silicon spectrum under the silicon spectrum, this is also the case

Platinum spark spectrum using the same type of platinum from which the frames of the silicon splinters are made

passed as electrodes. In fact there were a few platinum lines in the silicon spectrum

crept in, the elimination of which we succeeded easily on this, Weise. The results of the

Measurements of the silicon lines are given in the following table and are our parts

Changes to Rowland's normal spectrum, respectively to Kayser and Runge's Numbers

reduced. For the sake of comparison we give the visible parts by Salet and Plücker

found silicon lines and their wavelengths, as well as the lines indicated by Hartley

in the ultraviolet part of the spectrum. Refer to the Rowland's numbers in the third section

focus on the arc spectrum. It is noteworthy that the arc and fun

spectrum of silicon

is very similar; however, one of the main lines (2541) is strong in the spark, absent or weak in the arc.

It follows that, according to our research, we know the number of ten ultraviolet silicon lines of the spark have increased significantly, namely those extend from

we discovered new characteristic silicon lines a considerable distance further into the ultraviolet,

than was known until now; the most breakable ultraviolet silicon line from 'A

= 1929 became first

found by V. Schumann in Leipzig and we are through a private letter from the Lord Schumann was made aware of this line; we are including this line in our directory on.

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Table of the wavelength of the lines in the emission spectrum of silicon 1).1

Fun Irnnspectrum  
Internal,  
[I Salet2)

[Silicon spectrum by means of Plücker1

Remark

s Si Cl,

sity 1  
Si Si Cl4 Hartley

1 Eder

-----1

and Adeney and Valenta

the more breakable side of the spectrum a sharper one. As far as given by Ciarnician 2) i  
Drawing is to be judged, these should be those lines which Ciarnician 2) on a second spectrum  
of silicon, which spectrum is analogous to the Swan spectrum of carbon (5056 •  
should. The silicon line). = 15040 f is foggy when dealing with chlorosilicon at ordinary  
pressures

works, but when fluorosilicon is used in Geyser's tubes these lines become sharp  
and can be easily recognized as double lines 1). In any case, the one given by Salet is  
correct

Drawing does not match that of Ciarnician 2). To facilitate comparison, reproduced  
We see Salet's drawing in Fig. 21 and note that on the basis of the determinations of the  
wavelength

is carried out, while Ciarnician 2) only drew the spectrum image seen, which is why  
in the latter case the discussion becomes impossible as to whether foreign lines or  
connecting spectra in  
Ciarnician 2)'s silicon spectrum occur.

From the list of the silicon lines measured by us it can be seen first of all that the details of Said's and Plecker's already very uncertain in the blue and violet part of the spectrum become. This is due to the low optical brightness of these districts, respectively that of these districts lying silicon lines and due to the relative insensitivity of the eye to such colors.

The one from Salet with  $\lambda = 4129$  we found the silicon line given as a double line from the  $\lambda = 4129$  cell

$\lambda = 4131 \cdot 0$

length  $\lambda = 4128$  — likewise we found three rather strong lines at the beginning of the ultraviolet ( $\lambda =$

$\lambda =$

3905, 3862 and 3856) and numerous fine lines. The main lines are  $\lambda = 2881, 2631, 2541$  and the

highly characteristic band  $\lambda = 2528$  to  $2506$ , further the line  $\lambda = 2435$ . Up until now, the most breakable line of silicon found by Hartley was the line

$\lambda = 2435$ .  $\lambda = 2435$  Tir found numerous new silicon lines in the most breakable ultraviolet, which are shown in the table

are precisely specified. It is noteworthy that among these new most breakable silicon lines finds a main line next to a main band of  $\lambda = 2435$  cell lengths:

$\lambda = 2219 \times 5$   
 $2218 \quad 15$   
 $2216 \quad 76$   
 $2211 \quad 8$   
 $2210 \quad 9$   
 $2208 \quad 1$

$2122 \quad 8$  main line

The main line lags behind the main lines mentioned above in terms of intensity, but it does step back

both in the spectrum of elemental silicon, as well as when using chlorosilicon, etc., sufficient

clearly visible if the exposure was long enough.

After finishing our experiments with elemental silicon, we wanted to make sure that the lines which we have cited as silicon lines actually belong to this element, or whether

1) Anna L. d. Chern. u. Phys., 1873, 1  $\lambda = 1$ . Series, vol. XXVIII, p. 65 and Salet: "Traite de Spectroscopie", 1888, p. 203.

2) meeting area d. kais. acad. d. Wissensch., Vienna 1880, math. nat. - natural Cl., Vol. LXXXII, June issue.



J. M. Eder and E. Valenta.

strange lines had not crept in despite all precautionary measures applied. Therefore We subjected pure chlorosilicon and pure hydrofluoric acid 1) under various Conditions of a comparative investigation with the spark spectrum of the elementary Silicon.

The chlorosilicon was in a glass vessel provided with a quartz window, which was filled with dry Hydrogen was filled and which had previously been carefully dried 2), by means of a funnel tube allowed to flow in while the spark flashed. The vapor of the chlorosilicon is already decomposes at ordinary atmospheric pressure and gives even when a moderately powerful one is used Induction spark (without Leyden bottles) a relatively bright spectrum. The spark shows one blue colour.

The spark spectrum of chlorosilicon at normal atmospheric pressure also contains Silicon lines still lines which belong to the spectrum of chlorine 3). The emission spectrum of the Chlorine, however, never appears so conspicuously; the silicon spectrum always dominates. The chlorine spectrum must be eliminated, which is done by over-photographing a spectrum which is obtained when it is easily possible to let the spark from zinc electrodes strike with chlorine gas.

The spark in the chlorine gas under atmospheric pressure is bright: the line spectrum is angstroms, Plücker and Salet have been studied 4). The latter gives Fig. 21 (see p. 76) and the wavelengths.

Further attempts at the Silicon to produce its spectrum with the aid of silicon chloride made in such a way that the silicon chloride is placed in a spherical tube with a quartz window which was previously filled with dry hydrogen gas. As electrodes were, according to the method given by Bunsen, used coal tips 5) cleaned, which with a dropping device were dripped with silicon chloride during the sparkover. Under Under these circumstances we obtained by means of a large amount of fame without the use of Leyden bottles good spectrum photographs with an exposure time of 1/4 to 5/4 hours.

If strong bottle sparks are used, the linear one also arises in the case of chlorosilicon vapor Spectrum of silicon, as if one were working without the Leyden bottles. In the former case only kick

5056 \

the less breakable lines in). = {

5040 f and). = 4565 somewhat clearer, respectively as broad lines

and thus, at least as far as the ultraviolet spectrum extends, there is no reason for the  
To assume the existence of a second silicon spectrum for weak discharges.

The spectral lines of the appear in the hydrogen atmosphere saturated with silicon chloride vapor  
Hydrogen almost completely back, the silicon lines dominate and even become in this way  
get the most breakable silicon lines. However, the dimensions of the apparatus had to be  
kept small

because the chlorosilicon vapor in thicker layers has an absorbent effect on the more breakable  
ones

exerts ultraviolet rays of the silicon spectrum, making the lines of the more breakable part strong  
be weakened.

A survey of the spectral lines obtained in this way in an H atmosphere reveals  
first the appearance of hydrogen lines in the red of the line H $\alpha$  ...  $\lambda = 6562$  and the  
strongly broadened lines in green: H  $\beta$  ...  $\lambda = 4861$ , blue: H $\gamma$  ...  $\lambda = 4340$ , indigo: H $\delta$  ...  $\lambda = 4101$ .

1) Obtained from Dr. Th. Schuchardt in Görlitz.

2) Traces of moisture are the cause of the formation of silica, which steams up and makes  
the vessel walls cloudy

makes. For a more detailed description of the apparatus see p. 62.

3) In the presence of air, the air spectrum is added, and in the case of the operation in a  
closed vessel

is carried out, subnitric acid (NO<sub>2</sub>) occurs, which fills the vessel after a short time and becomes  
disruptive

Absorption phenomena can give rise to.

4) Combustion of chlorine in oxygen or of chlorine and hydrogen does not give a line  
spectrum.

5) cf. about this, as well as about the experimental arrangement, our treatise.

The emission spectrum of silicon.

As is well known, these broadened lines always arise when the induction spark is caused by  
hydrogen

at ordinary atmospheric pressure, and Salet gives a clear picture of this phenomenon in FIG.

On the heliographic reproduction of our spectrum photography, some of these are strong  
broadened hydrogen lines clearly visible.

If furthermore the spectrum of the zinc, respectively the carbon (depending on the electrodes  
used)

and the chlorine is eliminated, which can best be seen by taking pictures side by side with  
the Loky

If the split bar happens, the silicon remains, which is associated with the spark spectrum of the  
elementary

Silicon (silicon electrodes) is identical. The one made of silicon chloride by means of zinc  
electrodes in one

The silicon spectrum obtained in a hydrogen atmosphere and the comparative spectrum of zinc in hydrogen shows Plate IV, Figs. 1 and 2 1).

Although in general the spectrum of elemental silicon and that of silicon chloride are identical, if a strong induction spark is used, they still fall below Circumstances in the chlorosilicon spectrum characteristic broadening of individual line groups of the Silicon spectrums, as well as change in the relative brightness of the lines.  
The silicon double line r

4131 · 0}

} = 14128 .2 appears more clearly in chlorosilicon vapor than in electrodes in air. Something like that

applies to the three characteristic lines in violet, namely } = 3905, 3862 and 3856; these lines are in the spark spectrum of silicon, which is obtained between silicon electrodes in the air, present, albeit not very conspicuous because of the strong air spectrum, as they are not in and of themselves

are very strong. These lines already appear in chlorosilicon vapor in a hydrogen atmosphere

in the spark without the Leyden bottle stronger, particularly strong and broadened when used

a strong bottle spark, so that these lines then become main lines of the first order. At the

The clearest and sharpest lines of silicon are obtained by using liquid chlorosilicon

Drip onto pure carbon electrodes (linden carbon which has been cleaned and made conductive according to B's method)

and let a powerful induction spark penetrate. This creates by an exposure time from 15 to 20 minutes a well-defined, beautiful spectrum of silicon, especially developed in the

The most breakable parts, which, when using elementary silicon electrodes, can only be found after 1 to

2 hour exposure. This kind of production of the silicon spectrum is so excellent

for the breakable end is not suitable for studying the blue-violet rays and those of the

The beginning of the ultraviolet because it is very powerful. Carbon bands (namely the cyan bands)

partially obscure the silicon spectrum.

If hydrofluoric acid is used, the ultraviolet part is obtained

Dripping acid on carbon electrodes in a hydrogen atmosphere while the spark flashes over,

very few lines that belong to silicon. In particular, the most breakable part is absent

almost all the silicon lines, which is probably due to the large amount of water in which the

Silica fluoride is dissolved and the associated decrease in temperature of the spark and dilution

the liquid is likely to have.

1) In our table, the two comparative spectra are not printed directly next to each other and this happened with

Consideration of the shape and arrangement of the picture. For the purposes of measurement, these spectra are of course very close to one another been photographed.

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The ultraviolet line spectrum of elemental boron. Of

J. M. Eder and E. Valenta.

(Presented at the meeting of the Imperial Academy of Sciences on April 3, 1893.)

The emission spectrum of the elementary boron in the induction spark, as well as the spectrum of the through

The induction spark striking the vapor of boron chloride and fluoroboron is several times the subject of

Been investigations.

A look at the result of these experiments that preceded ours shows immediately that of the Line spectrum of boron only a few green lines in the visible part, and only three lines in the ultraviolet part

are known with regard to their wavelength and that of the position of other undoubtedly existing boron lines

There is uncertainty.

We owe the first information about the spectrum of boron to Troost and Hautefeuille 1), which let the induction spark penetrate through an atmosphere of chloroboron and fluoroboron and let in Spectrum consisting of numerous lines received, the lightest lines of which are two double lines in green

and were a double line in blue; in the ultraviolet, Troost and Hautefeuille give a canceled effect

Spectrum on. Wavelength determinations are completely absent from this information.

Salet 2) also examined the spectrum of the spark generated by chloroboron and fluoroboron, but could not get lines that were sufficiently sharp for wavelength measurements. In the former case

the spectrum of chlorine dominated, in the latter case the spectrum of that which was present as impurity always appeared

Silicon, which made the test results uncertain. One in these investigations Salet considered the yellow line (from), = 581 [?] to be characteristic of boron. It is

Salet succeeded in measuring the flame spectrum that burned with hydrogen in the air

To accomplish chloroboros, respectively fluoroboros. The green flame of the burning boron compounds

gives a clear spectrum of bands, which, however, is not attributable to elemental boron but to boric acid

comes to.

While Salet obtained no results with regard to the spectrum of elemental boron, succeeded Ciamician 3) the production of a boron spectrum by placing pure fluoroboron in a platinum retort, free from Silicon, and let the steam strike the spark.

1) "Compt. rend. ", 1871, vol. LXXIII, pag. 260.

t) Anna l. Chim. Phys., 1873, Series IV, Vol. XXVIII, pag. 59.

3) meeting area d. kais. acad. d. Science in Vienna, mathem.-naturw. Cl., Vol. LXXXII, 1890, July.

The ultraviolet line spectrum of elemental boron.

In addition, Ciamician received the same spectrum if it had a strong induction spark (but without Leyden bottles 1) between electrodes of graphitic boron in a hydrogen atmosphere overturned; he describes the line spectrum of boron as consisting of several green and a purple line. If you work with fluoroboron and use weak currents without a bottle charge, a second band spectrum is supposed to appear after Ciamician, which is supposed to belong to the boron and consists of shaded bands. The wavelengths are according to Ciamician:

For the line spectrum

\ =

green  
violet

of boron

5103  
{4981  
4966  
4964  
3596

For the band spectrum of boron I

4985  
4962  
I 4943  
(4243  
j 4192  
II  
4166  
4122

The only more breakable boron line, which Ciamician calls the violet line, has its own

According to information (see also above) the wavelength of  $\lambda = 3596$ . This wavelength in Ciamician's original

treatise is in any case with serious errors (probably misprints), because Ciamician saw a dark purple line, while the wavelength 3596 belongs to a line which is far in the ultra

violet, so it cannot be visible. Also the drawing of the one in question given by Ciamician

The line in the Boron spectrum does not coincide with the wavelength 3596, because the last two, just a moment ago

Ciamician uses visible calcium lines (presumably  $\lambda = 3969$  and  $\lambda = 3933$ ) in his drawing

further towards the breakable end of the spectrum than the boron line in question. The determination of the waves

The length of this line is therefore not very useful on the basis of the data, and we have it

half of this uncertain line was deleted from the list of lines known up to now.

As a result, our previous knowledge of the emission spectrum of boron is reduced to one green single and one green triplet line. Hartley 2) gives only brief information about this

ultraviolet spectrum of boron before; the same stated that a line of), = 3450  
· 1 and a double

(2497 O)

line  $\lambda = \sim 496$ .? ~ are characteristic strong lines, which belong to the boron.

| ~ ~!

In our investigations into the spark spectrum of elemental boron, we made use of

crystallized boron (the so-called Bor diamanten), which we find in beautiful, about 1 x 5 mm long

Krystallen from Mr. Hofrath Prof. Dr. A. Bauer was kindly made available. The attempts

Obtaining measurable spark spectra with such Bordiamonds initially failed, since these

Crystals are bad conductors of electricity, and therefore the spark, instead of from crystal to crystal, mostly

flipped over from the initially used platinum setting of one to the platinum setting of the other crystal.

The platinum setting turned out to be unusable because of the numerous strong platinum lines

- obscured weak boron lines.

That is why we left the boron crystals like diamonds, as they are used for cutting glass should be set in pure lead so that half of the crystals protruded from the socket. The induction spark

Under these conditions there is a good spectrum of boron, of course in addition to the

1) According to Ciamician, the boron spectrum should not appear between boron electrodes as soon as Lcydener bottles are switched on; in this case one should only see the hydrogen spectrum.

•) Proceed of the Royal Soc., 1883, Vol. XXXV, pag. 301.

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Lead lines. Since the spark washes around the boron from all sides, so much is carried away by the latter that the production of spectrum photographs with well-developed boron lines was made possible.

The conditions for the success of the experiment are that a very powerful induction spark is used; we worked with the one supplied by the "Wiener Elektrizitäts-Gesellschaft" Dynamo current (direct current), which is brought to 6 amperes at 110 volts through resistors had been.

The primary spiral of our Ruhmkorff 1) had a winding of 320 \ Nindings (length of the Wire: 82 m, thickness: 2 x 5 mm); the secondary spiral had a winding of 52800 turns (length of the wire: 14000 m, thickness: 0.17 mm.

Since the lead undergoes rapid oxidation under the action of the induction spark in the air, the experiment had to be carried out in a hydrogen atmosphere 2), whereby the numerous disruptive air lines have been eliminated. To eliminate the lead lines that line the boron spectrum enforce, we photographed the spark spectrum of the same lead (without boron) with the same length

Exposure time below the previous one.

Since the Bore diamonds also contain aluminum, the main lines appear in the spark spectrum

of metallic aluminum, which were also eliminated by secondary photography; the same thing applies to the coal lines, of which we only received traces, by the way. In this way it worked us to determine the boron spectrum with certainty by eliminating the foreign lines.

Even with relatively very short exposures (a few minutes exposure time), the Spectrum photography in the ultraviolet shows the strongest boron lines, namely the lines from the Wavelengths:

$\lambda = 3451 \times 3$

$\lambda = 2497 \times 7$

$\lambda = 2496.8$

which must be designated as the main lines of boron, in terms of photographic effectiveness far surpass all visible boron lines, so that one can say: the essential and characteristic in the main lines of boron lie in the ultraviolet. Below these lines is the

(2497.7)

Double line  $\lambda = 2496.8$  is the strongest in the whole spectrum. Most other ultraviolet boron

lines, which, although not as intense as those mentioned, are nonetheless characteristic. Main lines of the boron spectrum must be viewed, occur during the spectrographic recording

much earlier here before, as the few visible boron lines in which the boron spectrum is aligned with the spectrum of the

Silicon and carbon behave similarly.

The other ultraviolet lines of boron, the wavelengths of which are specified in more detail below, extend far into the ultraviolet. The visible spectrum of Boron is both number and strength of the lines as far as lines are concerned, subordinate to the ultraviolet spectrum.

The table below contains the list of those lines which our investigations have shown to the elementary boron in relation to Rowland's, Kayser and Runge's respectively. Normal numbers of the wavelengths. In addition to the 7 already known, we have found 14 new boron lines,

so that the number of currently known and assured with regard to their wavelength. Lines of elemental boron was thereby increased to 21. The majority of the boron lines exist from double lines which are very distinct and peculiar to the ultraviolet;



- 1) Obtained from Kaiser and Schmidt in Berlin.
- 2) On the experimental set-up, see p. 58 of these papers.

The ultraviolet line spectrum of elemental boron.

only one main line ( $\lambda = 3451 \cdot 3$ ) could not dissolve with and therefore had to, as well like the weak boron line ( $\lambda = 2388 \cdot 5$ ), run as a simple line. In the following table are next to According to our information, the wavelength measurements of Ciamician's and Hartley's for greater clarity for the sake of it.

Since the photographic reproduction of the spectrum of the lead-edged Boron diamonds because of the large number of foreign lines present, as well as that by means of carbon electrodes and boric acid

The generated spectrum is completely lacking in clarity, so we have to the heliographic reproduction waived. However, we will give a typographically reproduced one below Drawing of the boron spectrum, namely the scale parts give the wavelengths in Rowland's Units.

Line spectrum of the elementary boron.

Ciamician  
Eder  
and Valenta  
Hartley Lines  
intensity

$\lambda$ ;  $\lambda_{\text{R}} \setminus \lambda_{\text{R}} 5103$

1

4981 1

4966 1

4964

{

{

3957 9

3941 7

3829 3

3824 5

1

2

2

1

1

3450 6 3451 3

3246 9

6th

1

Main line

$(2689 \cdot 0 \setminus 2686 \cdot 2 \setminus 1$

$2497 \cdot 0 \setminus 2497 \cdot 7 \setminus 10$

2496 2

{

2496 8  
 2388 5  
 2267 · 0  
 2266 4  
 10  
 1  
 2  
 2  
 } Main! Lines  
 } Main lines  
 (2088 8 2 t 2088 4 2  
 (2066 2 2  
 \ 2064 · 6 2

According to our experiments, the spectrum of elementary boron appears in the strong induction spark

(Bottle spark) on; we cannot therefore endorse Ciamician's statements, which says that the boron spectrum appears only in the induction spark without Leydener bottle. The reason why Ciamician the boron spectrum in a hydrogen atmosphere in the bottle spark did not like probably in the fact that the bright hydrogen spectrum blinded him and he therefore the boron spectrum overlooked. When using the photographic methods we could spark in the bottle always easily detect the boron spectrum.

Following our experiments with elemental boron, we studied the spectroscopic behavior of boric acid in a strong induction spark.

We observed that, depending on the strength of the spark and depending on the experimental setup, from aqueous boric acid solution both the spectrum of compounds mentioned by Leconte that can receive boric acid, as well as the spectrum of elemental boron

86 J. M. Eder and E. Valenta, The ultraviolet line spectrum of elementary boron.

Induction spark (without bottle) with the help of a fulgurator through aqueous boric acid solution is created the spectrum of compounds of boric acid. The experimental setup can look like Leconte's ~ ~ Attempts are made 1).

At the lower temperature prevailing here, the spectrum of compounds of boric acid occurs, which is identical to the band spectrum of the boric acid flame 2).

Also the one between carbon electrodes, which are filled with boric acid solution (preferably with a little hydrochloric acid acidified) are moistened, the Borsa shows a weak flashing induction spark (without bottle) or e-band spectrum, though more indistinct than the same when the spark was jumped over into the aqueous boric acid solution.

However, if charcoal has been cleaned and made conductive by annealing, 3) with concentrated re111er aqueous boric acid solution impregnated in a hydrogen atmosphere to the aforementioned vigorous

When exposed to induction sparks from six L e y den er bottles, one obtains the spectrum of the e l e m e n t

a r e n boron 4). The boric acid undergoes complete cleavage in this experiment, and you receives all boron lines with great clarity. To carry out this experiment, we served and a relatively very pure boric acid 5). This was dissolved in water to saturation and thus the carbon electrodes cleaned as described are temporarily dripped. It now became a bulky induction spark,

by using a strong Ruhmkorff, six L e y den er bottles and a stream of 2 amperes and 110 volts obtained, flash through between the electrodes in a hydrogen atmosphere

calmly. The almost white light of the spark gave a spectrum in the quartz spectrograph, about, respectively under which to eliminate foreign lines on the one hand that under the same circumstances

produced normal spectrum, on the other hand the spectrum of the carbon electrodes (with distilled water

humidified in a hydrogen atmosphere).

It is remarkable that in the visible part of the spectrum this in and of itself is in this

Districts very weak and uncharacteristic Boron spectrum is hardly noticeable, while in the U l t r a violet all main lines of boron emerge with full sharpness and clarity.

When using a very weak induction current (inductorium in a short winding) the boric acid spectrum, if an aqueous boric acid solution acidified with hydrochloric acid and carbon electrodes, as described, used, also to the fore, although this reaction is mostly indistinct

occurs. When using a powerful inductorium and six Leydener bottles, like us Arrangement described gives boric acid, in concentrated aqueous solution on carbon electrodes dropped, the line spectrum of the elementary boron. The same is in the visible part, since it is of the

strongly broadened foreign lines (coal) is influenced, although not quite clearly, but the

The main lines of boron described above are particularly evident in the ultraviolet, even in the most breakable part

of the spectrum. In this most breakable part the boron reaction is particularly sensitive, and it appears

hence this spectral reaction for study, as well as for the spectrographic evidence of boron in compounds

especially suitable.

1) H. W. V o g e l: "Practical Spectral Analysis", 1889, I. Theil, p. 96.

•) Will be discussed in detail in a later treatise.

3) cf. p. 58 of these treatises.

4) Dry boric acid and coal give weak boron spectra with difficulty.

· ') Obtained from Dr. Th. Schuchardt in Görlitz.

The flame spectra of the alkali and alkaline earth metals first described by Bunsen and Kirchhoff were thoroughly tuned in the visible part by Lecoq de Boisbau with regard to the Studied the wavelengths of the characteristic lines; in the work of the aforementioned researcher: «Specters lumineux »(Paris 1847) there are also excellent spectral panels, which are based on hand drawings are made by means of copperplate printing.

While the visible flame spectra of the alkali metal and alkaline earth metal compounds have long been well known and are used in elementary chemistry classes, the course of these extremely important flame spectra in the ultraviolet has so far remained completely unknown.

The complete knowledge of the entire course of the flame reactions of the metals in one Bunsen flame across the visible and ultraviolet spectrum appeared to us not only of importance in itself, but also deserves attention because it draws conclusions on the emission spectra of metal vapors and the vapors of metal compounds with relatively very low temperatures. There are also the compounds of the alkaline earths partially dissociate in the Bunsen flame and mixed spectra of metals and their oxides, respectively give chlorides, these reactions require careful study in the ultraviolet part, about the views gained up to now on the basis of the knowledge of extensive spectral districts to be able to rectify. On the other hand, the relationship is that of the relatively low one Temperature of the Bunsen flame occurring ultraviolet metal lines with the main lines of the same Elements in the electric flame arc or induction sparks based on comparative spectral photographs to consider.

We therefore undertook the experiments described below. The greatest difficulty in making spectrum photographs of the flame reactions makes the permanent preservation evenly brighter, Bunsen flames colored by metal salts.

We have the means recommended so far to keep one with salt vapors for a longer period of time trying to get pregnant flame to apply 1). For the stated purpose wurden in particular curved glass tubes filled with salt solutions, at the lower end of which fine platinum wires are wicked

1) cf.: Kayser: • Textbook of Spectral Analysis,, 1883, p. 78.

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protruding, which always remained moist and were washed around by the flame, recommended; It showed but that this facility usually fails after a few minutes, so is by no means usable for a burn time of 6 to 24 hours. Goüy's method 1) which consists in using a so-called "refractor" to create a jet of finely atomized Blowing saline solution into the Bunsen flame gave neither sufficient lasting nor correspondingly bright Flame spectra. Therefore, after many attempts, we have the one shown in the drawing (Fig. 22), The apparatus described below is designed to meet the requirements set by us

corresponds perfectly and the achievement of evenly brighter bunsen flames, with any salt solution colored, allowed for an exposure time of 6 to 24 hours.

The apparatus essentially consists of a heavy pedestal (p) cast from metal, which is the Bunsen burner which can be rotated around a vertical axis and is provided with a platinum ring, or better Terquem burner (b), and the adjustable, inclined at an angle of  $45^\circ$  to the horizontal

Double disc (s), made of nickel metal, carries. This disc Fig. 22.

consists of two metal plates, between which the platinum wire mesh (n), braided from very fine platinum wire, pinched is, so that it is over the circumference of the disc 2 to 3 cm protrudes and into the saline solution in the vessel (g) immersed. The disk (S) is centered on the axis (a) and thus connected cone (c) by a clockwork in rotation offset. The platinum mesh passes the tub (g) and comes

•

g always impregnated with saline solution at f with a bunsen flame in touch, creating an evenly bright, through the metal salt in question colored bunsen flame arbitrarily long can be preserved if only the clockwork always pulled up at the right time and the tub (g) always with you Saline solution is obtained filled. The access to air at the The flame of the Terquem burner (b) must be regulated in this way that the lower blue cone of flame becomes sharp and above that the non-luminous, almost colorless one upper gas flame towers high. The ones to be examined if possible Salts must be on the border of both flames

partly introduced at f, that is, the platinum network must pass the flame at this point and it is allowed to only the light of the upper part of the flame can be used for spectrographing, because this Light is free from the Swan carbon bands. Would be the lower cone of blue rays too Sending light into the spectral apparatus would result not only in the visible part but also in the Ultraviolet many carbon lines occur next to water bands and the weak metal or metal oxide spectra, which arise from the flame reactions. The upper, almost colorless part The Bunsen flame, on the other hand, only emits the spectrum of the water vapor which binds water can be seen on all of our heliographic spectral tables.

This was first described in the memoranda of the Imperial Academy of Sciences<sup>2)</sup> Observation showing the separation, respectively elimination of the Swan spectrum from the

In order to guarantee us a flame reaction also in the ultraviolet part, this was done when this was carried out  
Attempts used.

- 1) Anna L. d. Chimie, 1879, vol. XVIII (5), pag. 5.
- 2) cf. page 1 of these treatises.

Bunsen's flame reactions in the ultraviolet spectrum.

While observing these precautionary measures and the described simple device'. Gelärg  
it is easy for us to see the flame spectra of the alkali metals, alkaline earth metals and the  
'Bötsälife  
to obtain many hours and thus long enough by means of the quartz spectrograph to achieve  
well-defined spectrum photographs down to the ultraviolet. The recordings I the

Spectra described below were made with a slit == 0.08 mm. (1

For the purpose of measuring the lines and bands on the spectrum photographs obtained in this  
way  
a comparison spectrum (spark spectrum of an alloy  
of zinc, cadmium and lead), which is also on all of the accompanying plates the spectrum  
shown is clearly visible.

1i, 1 1

1. Flame spectra of potassium, sodium and lithium salts.

a) potassium salts. .

By photographing the spectrum of the Bunsen flame filled with potassium salt vapors  
The knowledge of the spectral lines occurring in the same opened up to us against the stronger  
breakable end than was previously possible. For this purpose, however, was a 24-hour  
exposure time  
using a very bright quartz spectrograph with moderate dispersion is necessary, but  
the photograms allowed the course of the spectral reaction to be followed far into the ultraviolet.  
Kick it  
in the U l t r a v i o l e t the following potassium lines not yet observed in the potassium  
Bunsen flame  
on: the enormously intense main line of potassium  $\lambda = 4047$  Å, then the weaker  
potassium line A,  $\lambda = 4045$  Å  
and the line A =  $3217 \cdot 5$ . These ultraviolet lines in the luminous spectrum appear in the  
Spectrum photography quite sharp, but they cannot be resolved into double lines because  
they are the same  
In the flame spectrum are not differentiated between where mm. are more than in the spark  
spectrum and on the other hand  
the dispersion of our quartz spectrograph in view of this circumstance to their eventual  
Separation wasn't quite enough either.

The stated ultraviolet, which we found in the flame spectrum of the potassium salts  
Lines are also found in the arc and spark spectrum of metallic potassium as we move  
through

Parallel attempts have convinced.

The line, the length of which we determined with), =  $3217 \cdot 5$ , is without adoubt that of Kayser and { $3217 \cdot 8$ }

Runge in the electric arc spectra; around the potassium by means of G.it.terdouble line obtained} =  $132i: 7 \cdot 3 \{1;$

more breakable lines, some of which appear very forcefully in the electricarc; could<sup>11</sup> can no longer be found by us in the flame spectrum .; It seems that the sameonly at 1height're1 \ Temperatures such as is the case with electric arc lights and sparks' occur<sup>11</sup>, 1' as In general, these latter spectra also have more lines in the visible part than the Bunsen flame spectrum are.

If one compares the other occurring in the visible part of the flame spectrum of the potassium salts

Lines, as already described so excellently by L e c o c q, with 1 d'eii. fromK ayi'er and Runge found potassium lines in the arch spectrum; as well as with the lines' in the' spark spectrum of metallic potassium in a hydrogen atmosphere, 'it turns out that theseunien' all belong to the elementary potassium and evidently from the dissociation of the potassium salts in the flame originate.

The photograph of the spectrum of the flames of potassium salts shows a very strong and continuous one

Spectrum on; it begins (in the visible part) at about  $\lambda = 16,400$ , grows to  $\lambda = 5700$ , apparently remains constant until  $\lambda = 4800$  or  $\lambda = 4700$  and now gradually decreases until about  $\lambda = 4200$ , then it disappears, as 1 .: e c o c q first stated, for the eye until about  $\lambda = 4150$ ;

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The spectrum photography, however, shows that the continuous spectrum of the potassium salt flame is the

Has a maximum in the blue at about  $\lambda = 4800$  and from there, gradually weakening, up to against

$\lambda = 4000$  extends, then weakly, but still clearly perceptible up to  $\lambda = 3000$  extends, while the last tracks can be followed up to  $\lambda = 2800$ .

The continuous spectrum on which the potassium flame spectrum is based therefore extends

with a considerable intensity far towards the breakable end into the ultraviolet, that is to say much further than one assumed so far.

H. W. Vogel<sup>1</sup> was inclined to ascribe this continuous spectrum to potassiumoxide; we



but believe we can assume that this is not the case, as we continue the same Spectrum also elsewhere in the spark spectrum of the metallic in a hydrogenatmosphere  
Observed potassium.

On the basis of our experiments we have the whole Bunsen flame spectrum of potassium salts compiled in the following table.

Table of the lines appearing in the spectrum of the potassium bunsen flame.

Eder

to

Remark

s other

i Lecocq

Valenta

Roth ° '{7697

7663

7699

7666

10

10

) .fairly sharp line

7248-6825 7040 1 middle of a broad weak band

5831 5832 5

Yellow β {5803 5802 8) sharp line

5783 5783 5

Green 0 5342 5344 4 Center of a broadened line

5104

4948

5103

4950

3

3

t Center of a slightly broadened line

)

Violet γ 4045 4045 x 8 10 broad line; corresponds to the double line 4047 \* 4 to 4044 \* 3 of the arc spectrum

Ultraviolet{

-

-

3447 2

3217 5

4th

1

corresponds to the double line 3447 · 5 to 3446 · 4 of the arc spectrum \ newfor the

corresponds to the double line  $3217 \cdot 8$  to  $3217 \cdot 3$  of the arc spectrum /flame spectrum

As can be seen from the comparison of this table of the potassium lines of the Bunsen flame spectrum with the

The arc spectrum of the metallic potassium determined by Kayser and Runge appears, As mentioned, in the first spectrum some groups of lines are blurred and broadened; the latter Spectrum 'sich' sharp ffäh'El'ri .; The same is true of the flame spectra to be described later the alkalis and alkaline earths are the case.

b) sodium salts.

The sodium flame gives with an exposure time of 24 hours on average of the quartz spectrograph

except for the well-known yellow double sodium line - also ultraviolet, lines whose existence is in the

The flame spectrum of the sodium salts had hitherto remained unknown. In particular, the ultraviolet occurs

Sodium line  $A = 3302 \cdot 5$  and that  $A = 2853$  clearly and sharply; the light of the sodium flame, which applies to monochrome is therefore not monochromatic.

Hence, siq, h for the spectrum of the sodium Bunsen flame result in those in the following Lines indicated in the table.

1) H. W. Vogel: "Practical spectral analysis of earthly substances", Berlin 1889, I. Th., P. 144.

Bunsen's flame reactions in the ultraviolet spectrum.

Table of the lines appearing in the spectrum of the sodium Bunsen flame.

Eder and Valenta

yellow Ultraviolet{

N

• a

N / A

N / A

(5896

• T5890

.. 3302 5

.. 2853 · 0

--10

10

8th

2

corresponds to the double line  $3303 \cdot 1$  to  $3302 \cdot 5$  des Bunsen's flame spectrum (Kayser and Runge)

corresponds to line  $2852 \cdot 9$  of the arc spectrum

All these sodium lines appearing in the Bunsen flame are those which appear in the electric

Show flame arc in sodium vapor as well as in induction spark between sodium metal electrodes namely, they are lines which are easily reversed in the electric arc of flame. However, it does occur

only the less breakable lines in the flame spectrum, while the most breakable lines show which ones

in the bow and fun \ {enspectrum show up are absent. All sodium lines in the spectrum of the sodium bunsen

Flames belong, as the comparison shows, to elemental sodium.

In addition to these lines, the sodium flame gives a continuous spectrum, which is not so bright

is like the potassium flame and is fairly even, so that it is difficult to get the maximum to determine. This continuous spectrum is already Bunsen and Kirchhof in sight

---

bare parts; we determined the course up to the ultraviolet (see Plate VI), namely the flat,

Difficult-to-determine maximum a little further towards violet than is the case with potassium.

c) lithium salts.

In the lithium flame, two rather appear in the blue and in the ultraviolet after 24 hours of exposure

weak lithium lines, namely the lines  $\lambda = 4602 \cdot 4$  and  $\lambda = 3232 \cdot 8$

the two already known red and yellow-red lines. The entire spectrum of the lithium bunsen flame appears in the following table.

Table of the lines found in the spectrum of the lithium Bunsen flame. Eder and Valenta

J

Roth

Red yellow

6708 10

6103 3

Main line new for the Blue

4602 4 2 flame

Ultraviolet 3232 8 4 spectrum J

The lithium flame gives only a very weak continuous spectrum, by far the weakest of the alkali metals mentioned.

II. Flame spectra of calcium, barium and strontium salts.

a) calcium salts.

In the flame spectrum, the calcium salts appear alongside a few, as Le co c q 1) has shown in particular

Metal lines show numerous bands, which belong partly to calcium oxide, partly to calcium chloride.

1) Le co c q: "Specters lumineux", Paris 1874.

12 \*

J .. M. · Eder and E. Valenta.

By blowing hydrochloric acid into the flame, Mitscherlich and Lecocq succeeded in producing a number of calcium chloride bands to recognize and measure. Also by introducing an ammonia bead under the Chloride of calcium bead evaporating in the flame results in chloride lines<sup>1)</sup>. Our intention was to ensure the chlorine-calcium bands next to the chloride bands in the flame spectra of the calcium salts and to detect the appearance of such bands next to metal lines in the ultraviolet part.

By means of the rotary apparatus described, we succeeded in doing this with the use of calcium nitrate

Exposure for about 30 hours to photograph the flame spectrum of the calcium oxide down to the ultraviolet<sup>2)</sup>; we also photographed the spectrum of a calcium chloride flame, which is bright <; r, so; d: ass exposure of 20 hours was sufficient for recording; besides, we moved

d. the spark spectrum of metallic calcium in a hydrogen atmosphere in the circle of our Investigations and were thereby able to determine the bands of calcium oxide from those of the Chlorcalciums and the individual metal lines occurring in the calcium flame spectrum

to identify. 1

Tab ~ II ~ the iri. Lines and bands appearing in the spectrum of the calcium Bunsen flame.

In the table above are those lines (bands) which appear in the calcium salt flame spectrum occur, recorded and with the exact designation whether they correspond to calcium oxide, calcium

<sup>1)</sup> V ö g e l: "Practical Spectral Analysis", I. Th., Berlin 1889, p. 145.

<sup>2)</sup> The calcium nitrate flame is relatively very poor in light; the characteristic ones appear even under favorable conditions

Calcium oxide bands only weakly. Carbonate of lime is deposited on the platinum network of the apparatus, which forms the mesh of the network, whereupon the calcium oxide reaction occurs even worse. It is therefore necessary to add some calcium nitrate solution Add nitric acid.

Bunsen flame reactions in the ultraviolet spectrum.

chloride or elemental calcium. The calcium oxide and calcium lines occur in each

Calcium salt flame on, regardless of whether nitrate or chloride was used.

When using calcium chloride, especially when ammonia or hydrochloric acid is present,

Both oxide and calcium chloride bands appear, which are expressly stated in our directory are listed and in brackets.

Our wavelength determinations of the calcium oxide bands from  $\lambda = 6441$  to  $\lambda = 5644$  are correct

adequately agree with the Le Couc'schen information; because with the vagueness of the bands the

If the position of the maximum cannot be determined with certainty, these wavelengths are not even in the

fourth decimal place (1 Angstrom's unit) can be described as quite safe. The bands are smaller

Wavelength  $\lambda < 4644$  should be more certain on our spectrum photographs than with Lecocq, which

directly watched, be.

In the ultraviolet part we discovered a series of new, narrow calcium oxide bands, which are fairly evenly distributed. These bands are through the line  $\lambda = 4227$ , the elementary Calcium belonging, interrupted; in addition, towards the breakable end, there are narrow oxide bands

on a continuous, faintly shining ground, which is difficult to find or to be measured because the continuous spectrum covers the bands with longer exposure and with shorter exposure

Exposure, on the other hand, they become so weak that they can no longer be measured.

With correct exposure, some of these blurred ultraviolet oxide bands can be seen in dissolve a kind of double bands, two of which are always shining through a joint appear underground.

The table gives an overview of the oxide, chloride and Metal lines (respective bands) of Bunsen's lime salt flames; are under these lines (bands) 30 newly discovered calcium oxide bands.

b) strontium salts.

Strontium nitrate gives a good flame spectrum even with great dilution, but it is used

For our experiments we would have rather concentrated solutions, because only in this case the whole

Flame evenly and intensely red in color. A lot of salt vapors escape into the air, which (despite Ventilation) make the stay in the work room very uncomfortable, which is when using

Chlorbarium is not the case.

\, Vir obtained good spectra with exposures of 12 to 20 hours.

In the spectrum of the strontium flame the oxide bands appear very strongly in the visible part, in that the red bands in particular are very bright. In spectrum photography several strontium oxide bands appear in the ultraviolet 1), which, however, are far from being distinct stand back behind the ultraviolet limestone bands (as they are also less bright than the barium oxide bands are). It is the strontium oxide bands, however, with regard to their moderate width and vagueness similar to calcium oxide bands, but the latter are somewhat narrower and some of the Strontium oxide bands appear to be double bands. These are narrow faded bands fairly regularly distributed, embedded in a weak, continuous spectrum. The latter extends up to the first water band.

In the following we give a table of the lines and bands of the strontium flame spectrum, where, in a similar way to what happened with calcium, those corresponding to strontium oxide bands (obtained using strontium nitrate) as well as the strontium chloride bands

They are missing in the heliographic representation of the spectrum.

J. M. Eder and E. Valenta.

are bracketed, while the lines of the elementary strontium, which by dissociation of the Strontium salts are formed, are not in parentheses. The chlorstrontium flame gives a spectrum which contains all lines and bands in the table.

Table of the lines and bands occurring in the spectrum of the strontium Bunsen flame.

Ul. 'Flammer spectrum of boric acid.

In an earlier essay 1) we already have the emission spectrum of elemental boron described. In the following we drew the very characteristic spectrum of compounds of boric acid, such as

The same occurs with the hydrogen or fluorescent flame colored green by boric acid, in the circle of our investigations. This spectrum shows no lines of elemental boron; ~ it was already investigated earlier, but these investigations extended only to the visible part of it.

Th. Simmler 2) described the boric acid flame spectrum in the year 1860, as it is in the Boric acid (located on a platinum wire) green colored Bunsen flame can be observed. Hey

indicates three equally spaced green and one blue lines, of which the two are fewer

1) cf. p. 82 of these treatises.

2) Th. Simmler: "Jahrb. d. Graubünden natural research society. f. 1860 », from there passed into Poggendorf's Anna!., 1862, (4th row, vol. XXV, p. 250.

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breakable green lines (bands) the most intense. Presence of alkalis or alkaline earth metals does not hinder the reaction if sulfuric acid is added. Simm 1er found that by means of this spectral reaction

0 · 00119 / f boric acid can still be detected, but the turmeric reaction is more sensitive.

G. Salet (Traite de Spectrum, Vol. I, 1888, pag. 179) received brilliant broad bands in the spectrum

a hydrogen flame containing chloroboron, fluoroboron or boric acid; they appear in the Oxidation zone of the flame. The Bunsen flame also gives the same spectrum with boric acid. The maxima

the boric acid bands are included according to S a l e t "A = 640

620

603

B2 08 y ... 580

B2 08 c1. • • 548

B2 08 [~, "A = 520 B2

Oa ~..... 461

470

454

The spectroscopic behavior of boric acid in the Bunsen flame was also described by L e c o c q

de Boisbeaudran 1) very precisely; he heard some boric acid in the flame using fine platinum wire

of the Bunsen burner and measured the nicely defined boric acid bands.

As the most characteristic, he gave the bands of "A = 5480, 5807 and 4941 (the

other bands measured by L e c o c q are listed in our table below). \ While that

, The flame spectrum is very clear, says Lecocq of the spark spectrum of a boric acid solution,

that the latter is weak and shows the boric acid bands of the flame spectrum 2). These latter

emerge clearly when a trace of hydrochloric acid is added to the boric acid solution.

The ultraviolet spectrum of the green boric acid flames had not yet been examined, which is why we have included it in the scope of our investigations, in anticipation of new ones to obtain ultraviolet, highly breakable lines or bands or a possible connection to be found between the boron spark and the boric acid flame spectrum.

Our experiments have shown that the spectrum of boric acid compounds is only pure in boric acid flame occurs both in the flame of a solid boron located on platinum wire

acid-fed bunsen burner, also; also, and better, in a colorless luminous gas or water

material flame, which is fed with boric acid ethyl, is a medal. The green achieved in the latter cases

Flame is very high and gives regular broad bands, the course of which is violet and ultraviolet

have studied in depth.

\ Vir obtained when using luminous gas impregnated with boric acid ethyl, which is

Linneman's blowers, using oxygen, were burned for one hour

Exposure six new violet and ultraviolet bands, which regarding their character and rel

Lich the regular distances from each other are similar to the visible bands. Even with increased Pressures of the oxygen flowing into the boric acid flame (up to 20 cm of mercury) and 3 hours

After exposure, we did not get any further bands of shorter wavelength. The experimental set-up was such that such more breakable bands could in no way escape observation,

since even the low-light water band ( $H\gamma$ ), which extends far into the ultraviolet, was clearly visible, without a boric acid band being seen on the plate in this more breakable area.



1) "Specters Lumineux", 187.Jc, p. 191.

In the case of a strong bottle spark, only the spectrum of elementary boron occurs as a result of the splitting of boric acid. (Eder and Valenta a. a. 0.).

But these flame reactions in the ultraviolet spectrum.

The spectrum of boric acid compounds shows only less breakable bands, of which the characteristic ones lie in the visible part; the main band is the band located at  $\lambda = 5478$ .

From there the bands extend over the violet and gradually weaken until the beginning of the Ultraviolet. The bands are wide and almost evenly shaded on both sides. Only with the Band ( $\lambda = 5478$ ), a clear, strong line was found in the middle of the band and no lines appear in any of the others. It is noticeable that the connection spectrum of the Boric acid has no short-wave bands or lines, while the spectrum of the elementary Boron shows its characteristic lines precisely in the more breakable part and in the strongly breakable ultraviolet.

Table of the lines and bands appearing in the boric acid flame spectrum.

Eder  
Salet Lecocq and  
Valenta

Absorption spectra of colorless and colored glasses taking into account the ultraviolet. Of

J. M. Eder and E. Valenta.

(Presented at the meeting of the Imperial Academy of Sciences in Vienna on May 4, 1894.)

The absorption of colored and ultraviolet light through glasses of various types Composition deserves special attention because of the use of different types of glass for optical and especially for photographic purposes, often due to their transparency appears conditional to light rays of different wavelengths. This applies in particular of the new Jena glass types, which are produced in the glass smelters of Schott and comrades in Jena produces and, in addition to other optical purposes, also extensively for the production of photographic lenses can be used.

While the data is known for the refractive power of these glasses, it is not the case 1) with regard to their permeability to ultraviolet light rays.

As is well known, common crown and flint glass with regard to their absorption capacity for ultraviolet light behave very differently, so the investigation of the new types of glass is of interest in this direction, which is not of the practical background for objective generation lacks; this is especially true for the barite, phosphate, borate and zinc glasses, which of the above Institutes are established.

There is also no information about the absorption ratios of the glass fluxes colored by metal oxides related investigations, at least no such investigations on the composition of the glass flows, which served as the starting point in the manufacture of the glasses was taken. For this reason we carried out the following series of tests.

1) The investigations of Schjerner in g «On the absorption of ultraviolet light rays by different glasses» (Berlin 1885, inaugural dissertation) deal with the older crown and flint glasses. Schjerner in g used to his Investigations of a concave lattice of 3 x 9 m radius of curvature and bromide silver gelatin dry plates; he served as a source of light Sunlight. In this work those glasses proved to be the most permeable to ultraviolet light, which were the least specific gravity possessed; however, Schjerner in g himself says that this rule has no general validity as soon as the Glasses show a different chemical composition. Since at the time of the work Schjerner in g's the Jenenser glass types, which today play a major role in applied optics and in which the chemical composition of the Glass is a very variable, nonexistent<sup>1</sup> so these investigations are irrelevant for our own work i;

Absorption spectra of colorless and colored glasses.

1. About the absorption of ultraviolet light in colorless glasses.

The material for the experiments on the absorption of ultraviolet light in colorless glasses was kindly given to us by Dr. Schott in Jena. The glasses were in plane-parallel discs each 1 cm and 1 mm thick cut, ground, polished and then in front of the Slit of a quartz spectrograph brought. The light source between electrodes from a Alloy of lead, zinc and cadmium 1) flashing spark of a great fame k o rffian inductorium. The absorption spectrum of this light in glass was photographed on silver bromide gelatine plates; the exposure times were 1 to 10 minutes.

By comparing the absorption spectra of the thin and the thicker glass plates, one could see Gain a good overview of the different levels of absorption of the individual types of glass.

The types of glass examined can be seen in the following table:

Absorption in the thickness of Partial dispersion

Bre-Mittlere 11'11, 111, 101'11.111,

Fabrication-Dis-V =

cation designation n -1 entry entry

Index for person Beginning of the beginning of the no.D C to F

, 6, n a strong one strong

C-D D-F F-G 'schwa- (complete) schwa- (complete) check

off-off off-off-

sorption sorption sorption sorption " " " "1.

154 common silicate

Light flint. .. 1 · 57101 0 · 01327 43 · 0 0 · 00384 0 · 00943 0 · 00791 304

300 330 323

2. 103 common silicate

Flint. ... 1 62016 0 01 709 36 2 0 00489 0 01220 0 01041 314 301 340 328

3. 522 Baryta-Leicht-Flint 1 · 55536 0 · 01153 48 · 2 0 · 00334 0 · 00819 0 ·

00677 303 298 324 318

4,499 common silicate

Crown ... 1 · 51850 0 · 00885 58 · 6 0 · 00262 0 · 00620 -300 295 325 320

5.608 Crown with high dis-

ersion .. 1 · 51494 0 · 00943 54 · 6 0 · 00277 0 · 00666 0 · 00543 290 285

320 314

6. 225 light phosphate

Crown. . 1 · 51593 0 · 00737 70 · 0 0 · 00222 0 · 00515 0 · 00407 275 249 314

307

7.545 common zinc

Silicate Crown 1 · 51842 0 · 00886 58 · 5 0 · 00262 0 · 00624 -285 277 321

315

8. 245 barite-silicate-crown 1 x 50958 0 x 00 796 64 x 0 0 x 00 238 0 x 00

558 -285 276 322 316

9.560 English hard-

Crown. 1 · 51681 0 · 00857 60 · 3 0 · 0025300604 -296 279 325 320

The attached heliographic table shows a series of the comparative ones we have made

photographs of the absorption spectra of these glasses; those in the table above

The figures recorded are the mean of three test series.

As can be seen both from the panel figures and from the wavelengths of those rays of light from which the absorption asserts itself, as the table shows, behave the glasses are very different from the ultraviolet light.

The most unfavorable, that is, the least permeable to the ultraviolet rays, proved the ordinary silicate flint glass. The new barite flint glass absorbs in thin Lay the ultraviolet in the regions A = 300 fL fL, which is initially the Fraunhofer lines

P to T; in a slight degree; thicker layers of heavy flint glass already absorb the ultraviolet light

from K ab to a considerable extent, in the case of barite flint glass in a thicker layer, on the other hand, there is considerable absorption only with M or N.

1) cf. page 44 of these treatises.13 '

The absorption of barite flint glass in thin layers is almost the same as that of English Hard crown; in thicker layers, however, the opacity of the flint glass to the ultraviolet decreases faster than is the case with the aforementioned and other crown glasses.

The high-dispersion crown glass shows very satisfactory permeability for ultraviolet light (No. 5), as well as the zinc or boron crown glass; but all of these glasses exceed the light weight h o s p hat-Cr o w n g l a s (No. 6), which of all glasses has the greatest permeability for the ultraviolet

Light rays (from), = 300 nm) shows. However, this type of glass is relatively cheap despite its being Behavior nevertheless not remotely in terms of permeability for the ultraviolet with the quartz

compare, as is immediately apparent from the accompanying heliographic table, Figs. 2, 7 and 1.

Thicker layers of ordinary heavy flint glass (several centimeters thick) practice for rays from the beginning of the ultraviolet, even for the most breakable violet rays next to the woman nh

of e's line H ( $A = 496 \cdot 8$ ), an absorbing one, if weak, at least noticeable

Effect, while an equally strong absorption with barite light flint glass only with the lines M

or N occurs and in the case of Crown glasses about 0. The curve showing the absorption of the glasses at

increasing glass thickness against ultraviolet light, increases in any case for all

Flint glasses faster than with the

Fig. 23. Crown glasses, namely with the A aß C

E F HK L M N 0 p Q

the former in all the greater degree, as the lead content grows.

$$|++ - r|1$$

1111 1 1 1 1 1! 1 1

The typical course of absorption of ultraviolet light

2

1111 1 1 1 1! 1 1 1 1 1 in crown glass on one side and flintU.N

1. Absorption in flint glass. -2. Absorption in the crown glass. glass on the other hand shows the opposite Figure.

Since the lenses used for photographic lenses are usually cemented with Canada balsam and already made Hartle y's attention to the absorbing effect of this body, so we also included the Canada balsam in the circle of our investigations into light absorption. For this purpose we cemented two rock crystal plates with Canada balsam and photographed them. Spark spectrum of the metal alloy mentioned in a manner analogous to the determination of the absorption capacity

the glasses. It was found that the strongest absorption of the ultraviolet was approximately  $\lambda = 298 \cdot 0$ , that is behind the Fraunhofer line U, begins; it is thus the absorption for the strong refractive rays are less than with the best 1 cm thick glasses, somewhat larger than with the

1 mm thick crown glass plates, on the other hand somewhat smaller than the 1 mm thick flint glasses (see above

Table). It shows that Canada balsam for glass lenses in terms of absorption in the ultraviolet is a completely harmless cementing agent, because its related absorption capacity is such is that it would only come into play with those highly breakable ultraviolet rays, which are absorbed by the glass anyway. On the other hand, Canada balsam in their permeability to ultraviolet severely damaged and as to their efficiency on that of

Glass bodies pressed down, even if the thickness of the cement were only 1/10 mm. Thick Glycerine, which is already V. Sc human n as a binder for quartz prisms for the purposes of spectrum photography

recommended, on the other hand, is so permeable to the ultraviolet rays that the spectrum up to the zinc line),  $\lambda = 2024$  penetrates without weakening, like the attached heliographed plate (VIII),

Fig. 20 shows.

The question now is whether with photographic lenses working in daylight quartz lenses versus glass lenses

would prove considerably advantageous, assuming that the photographic objectives would have the same relative brightness (ratio of the effective aperture to the focal length). To this

Absorption spectra of colorless and colored glasses.

For the purposes of this, we compared a simple plano-convex quartz lens with a simple one with the same glare reduction

Crown glass lens (Focus for the Fraunhofer line D =  $75 \cdot 111$ ) by adding both to photographic Used recordings in diffuse daylight. It turned out that the practical photographic

Effectiveness on silver bromide gelatin plates is almost the same. The quartz lens is a bit more luminous, which However, the difference was hardly noticeable 1). Remember that the glass lens is so much of the photographic absorbs strong ultraviolet, which passes through the quartz lens unhindered, so that is Result perhaps strange; however, this phenomenon soon finds its explanation in the circumstance, that daylight contains relatively few highly refractive ultraviolet rays and that is diffuse reflected Daylight, with which we usually have to deal in photographic practice, is poor Rays of less than  $11 \times 10^{-7}$  m (wavelength than),  $\lambda = 390$ . The rays of light that shed women Lines L to N correspond, play a minor role under these conditions, all the more so, than the maximum sensitivity of the silver bromide gelatin plates in the light blue of the spectrum between ( $\lambda = 438$  to  $\lambda = 430$ ) is 2); there now even the direct rays of the solar spectrum arise Silver bromide gelatine in the vicinity of the line M only express  $1/10$  of the effect in the blue and further there In the diffuse reflected daylight these ultraviolet rays appear even weaker, so explained make sure that the ultraviolet rays are of shorter wavelength than those of the women's courts Line M in the production of photographic images in the camera using bromide silver plates little consideration.

So it provides crown glasses for practical photographic work in diffused daylight both on its own, as well as with the use of Canada balsam, sufficiently permeable to ultraviolet Lenses, so that a substitute for these lenses with those made of quartz is not to be thought of needs.

It is different with heavy flint glass lenses; these have a noticeable effect in denser layers Absorption in the violet and a very strong one in the beginning of the ultraviolet. If you consider that the Light rays next to N have about half the photographic effect on silver bromide than those at the maximum of the effect (light blue next to line G), it is immediately evident that photographic Objectives that contain heavy flint glass as components, with the same relative aperture

Diameter)

(. will only provide half the photographic effectiveness of the picture, compared to simple ones

B.

racing worlds

such lenses, which consist only of crown glass; close to the crown glass, but not the same. The same applies to combinations which, in addition to crown glass, also contain barite light flint glass lenses.

This behavior of the glasses is important with regard to the ratio of the optical brightness on the photographic effect of the light image when using different types of lenses.

## II. Colored glasses.

The absorption spectra of the glass fluxes colored with metal oxides show in the visible, as well as in the ultraviolet part, a greater variety than the colorless glasses.

Here, too, there are no related studies on composition, color, Absorption spectra before.

We owe the material we examined to the friendliness of Professor Dr.

Left and Adjunct Adam at the k. k. Austrian Museum for Art and Industry in Vienna, which

1) Heavy flint glass lenses behave noticeably less favorably, just as ordinary achromatized glass lenses, which are made of Crown and flint glass are combined.

2) cf. O. Lohs e: "The effect of colors on silver-bromide gelatine plates". (Yearbook for Photography and Reproduction Technology for 1894, p. 271.)

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at our request, the glassware with the greatest care in the chemical laboratory of the ceramics

Established experimental institute. The glass flows were cut into sheets of various thicknesses, these ground and polished so that plane-parallel glasses of 1 mm and  $\frac{1}{2}$  to 1 cm thickness resulted,

which served as the starting point for our investigations.

The examination of the absorption spectra in the visible part was carried out with the help of a Kruss

Spectroscope, the scale of which was converted to wavelengths while we were investigating of the ultraviolet as well as the yellow to violet part of the photographic method.

The photographed spectra extended there we used orthochromatic (erythrosine) plates, up to the Fraunhofer line D, whereby a control of the direct readings on the Spectroscopes, which we made, was made possible.

These comparisons clearly showed the low reliability of the human eye for observations in the violet, for the absorption spectra visible from G to H, were because of them

Faintness of light so inconsistent with the photographic spectra that it is considered unreliable had to be eliminated from the observation series.

The glass masses used for the investigation were given by the aforementioned professors Dr. Linke and Adjunct Adam made in the following way: A set of glass served as the starting point, which corresponds to the composition  $2\text{CaO}$ ,  $1\text{K}_2\text{O}$ ,  $1\text{Na}_2\text{O}$ :  $10\text{SiO}_2$ . In this mix became a Part of the  $\text{SiO}_2$  is replaced by boric acid, creating a glass of the following composition after melting resulted:

A)  $2\text{CaO}$ ,  $1\text{K}_2\text{O}$ ,  $1\text{Na}_2\text{O}$ :  $8\text{SiO}_2$ ,  $2\text{B}_2\text{O}_3$   
 $1\text{RO}$ : ( $2\text{SiO}_2$ ,  $0.5\text{B}_2\text{O}_3$ ).

But since the color of the glass also depends largely on its composition, in particular from depends on the size of the lead content, lead glasses were also made for coloring, namely:

B)  $1\text{RO}$ : ( $2 \cdot 5\text{SiO}_2$ ,  $0 \cdot 3\text{B}_2\text{O}_3$ ), where  $\text{RO} = 0.32\text{PbO}$ ,  $0.52\text{K}_2\text{O}$ ,  $0.16\text{Na}_2\text{O}$ .

C) Formula as for B), but  $\text{RO} = 0 \cdot 82\text{PbO}$ ,  $0 \cdot 18\text{K}_2\text{O}$ ,  $1 \cdot 55\text{SiO}_2$ .

To achieve a pure yellow chromic acid and green copper glass, even pure lead glasses, produced from minium and sand, can be used, namely:

Only absolutely pure preparations, cobalt oxide, were used for coloring by the gentlemen mentioned self-produced cobalt oxide potash, nickel oxide from copper-free nickel vitriol, from which previously the not insignificant amount of the cobalt had been completely removed, was used. For coloring with manganese oxide, iron-free manganese oxide became one, and the same for coloring with copper oxide iron-free copper oxide is used.

The coloring with chromium oxide, chromic acid and that with iron oxide presented great difficulties, respective iron oxide, because in addition to the composition of the glassware. the height The furnace temperature and the nature of the furnace atmosphere influence the nuance of the resulting Take coloring. For example, glasses no. 13 and 14 in the table below made by adding 4% iron oxide to glass set B, only glass no. 13 was made in reducing Oven atmosphere (Coaks oven) and glass No. 14 melted in an oxidizing oven atmosphere (gas oven).

4l,, · •

~

... '.



Absorption spectra of colorless and colored glasses.

In any case, glass no. 13 contains oxide and differs significantly from glass in terms of color No. 14, which is an iron oxide glass.

The same was found when melting chrome glasses. Pure lead glass (D) obtained by fusing with chromium oxide exactly the same color as by fusing it with chromic acid potash, see above that it seems impossible to produce chromium oxide glass of this composition.

On the other hand

glasses No. 8 and 9, which correspond to formula A), showed a difference in color. The Glass No. 8 obtained by fusing it with chromium oxide appears pure green, while the medium-sized

Potassium chromate scored No. 9 glass appears more yellow-green, which would probably suggest that

the same also contains  $\text{CrO}_3$  in addition to  $\text{Cr}_2\text{O}_3$ .

In the following we give an overview of the colored glass flows: No. Cobalt

glass from set B with 1 ° fused in cobalt oxide

2 copper glass A, 3, copper oxide

The test results regarding the absorptions of Roth up to the beginning of the ultraviolet, which in the case of glass masses come into consideration at all because of the self-absorption of colorless glass

(this is up to the Fraunhofer line T), are compiled in the following figures. The

Curves, which express the course of the absorption, are on the Fraunhofer grounds

Lines (Conu) related.

In addition to the already mentioned glass flows, we have a number of colored glasses, which

Mr. Zettler, Director of the royal Bavarian Institute for court stained glass

made available in Munich. The examination result is at hand from

two figures with absorption curves (based on the Fraunhofer lines) in the following summarized.

1. Gold ruby glass (G 1 as flashed glass), see Fig. 24, No. 1. - Color bluish-red. - The maximum the absorption lies between D and  $\frac{1}{2}$  E. The absorption band extends on the one hand towards D, on the other hand against G. The gold ruby glass is for blue and violet, as well as for the beginning of the ultraviolet

highly permeable. Between the ultraviolet line N and O, one begins towards the more breakable end rapidly increasing absorption.

2. Copper oxide flashed glass (copper ruby), see Fig. 24, No. 2. - color red.

- Shows in

thicker layers an absorption up to over D. Thin layers show an absorption maximum at

D to 1/3 E, after which a clear green-blue shimmer of light appears a4f i,  
.mcj yrst V911j;) started hastily F

J. M. Eder and E. Valent a.

the absorption becomes total. Red copper oxide glass is not permeable to the more breakable rays,

which is why it is very suitable for the production of darkroom panes for photographic purposes.

3. Copper oxide glasses (colored in the mass), see Fig. 24, Nos. 3 and 4, can be used depending on the

Composition of the glassware appearing blue, blue-green to green in color.

Lead-free potash soda glass (Glass set

A) gives blue-green to

blue glasses, whereas lead silicate

Fig. 24.

Aa B C E f li K L 1,1 ll p Q take on glass-green colorations. The absorption ratios of these

Glasses are strikingly different. KalimU-  
colored with copper oxide.

L.J .... 1 - A-m\_\_\_; .\_. I\_\_\_\_\_J\_I --- 1 ... I\_\_II

\_L\_JII\_J\_I\_I\_IL\_j\_I1-LI\_j\_IIL 2 soda glass gives an absorption

ll ll 17fLI 11 1 1 1 JJI + fl:

graze in the red and leave yellow, green  
and blue light to near

U-.L.J .... 111I\I ~ I. I = L - = JkRI ~, \_j\_, \_  
I\_IIL\_j\_I\_L\_I\_L\_JIIL 3

G through; at G there is a small  
absorption band on what

4th

IJIN IV 11111111111 the absorption is violet G, 1/2 H  
reduced and at H

L .... J :: LI, .ITTI - .. 1 ..- 1 --- 1 ..... alL-d? == -----... 1\_-1 \_\_\_\_\_  
J\_I\_j\_IIL-5 quickly against the ultraviolet

--\_ --- ... L.L\_IJ // \_ L\_JII\_J\_I - 1 - .. IL\_j\_Iincreases. The lead

glass that comes with

Copper oxide is colored, indicates a

u .... w, .\_. tfil\_\_\_. I ~ IJ? r'----- i-\_L.I ....\_ 11\_J\_JII\_J\_I\_j\_I  
[ J\_I]

1 \_ .. J\_I\_J\_JIIL\_ 6 similar

absorption band as

the previous one in the red, it works 7th

trrll LYI 1111111111 but mainly yellow and green,  
on the other hand only a little blue

8th

[[1 II? R II 1 1 1 1 11 1 1 1 light through so that a vigorous Absorption already  
takes place in the blue  
and rising over 0

[IM YY I II 1 1 1 1 11 1 1 L✓

Extends violet and ultraviolet. In the  
case of lead glasses, the

10

WJ I JJ ;; L III U2f I I 1 1 1

Compare with the pure alkali glasses the  
absorbent strip

from the more breakable end of the  
Spectrums versus the less  
12 breakable moved.

rn1 LfEJ II 111 111 LJZ11

rn 112fb: I II 1TI 1 1 1 1 1

1

4. Chromium oxide glass, 1 ase r,

1. Gold ruby, red. -2. Copper oxide, red. -3. Copper oxide, glassware A, see Fig. 24, No. 5,  
by entering

blue green. -4. Copper oxide, glass set D, green. -5. Chromium oxide, glass set fl,  
green. -6. Potash chromate, glassware A, yellow. -7. Potash chromate, glass of  
Chromium oxide in molten

set D, yellow. -8th. Chromic acid copper oxide, glassware A, blue-green -9. cobalt

Glass flows are green and

glass A, blue. -10. Nickel glass D, brown-yellow. - 11. Manganese, glass set B,  
violet. -12. Manganese, glass set D, violet. though of purer green (grass green)  
as copper oxide glasses. The

The absorption band, which extends from red to yellow, usually shows two weak maxima at B and C against D. Yellow and green light pass through almost without being weakened.

With the woman nh

The absorption begins of e r's line F, which slowly rises to the blue (at G); at intense With colored glasses, strong absorption already occurs in the blue and violet, with weakly colored glasses (especially for ordinary soda glasses free of boric acid) the mean absorption ranges from E to H; you only becomes strong in the ultraviolet (see dotted curve).r

Plate VII.

Bunsen's flame reactions in the ultraviolet spectrum. .

1. Flame spectrum of boric acid. -2. Flame spectrum of the barite salts. -3. Flame spectrum of the strontium salts. -4. Flame spectrum of calcium nitrate.5. Flame spectrum of calcium chloride.1

T

Absorption spectra of the nitro and  
amidocers. Of

J. M. Eder.

(Presented at the meeting of the Imperial Academy of Sciences on May 20, 1897.)

The absorption spectra were observed by means of a Krs spectral apparatus (with a light flint prism), and in view of the great permeability of the blue and violet glass beads used, the absorption bands could also be observed well in these areas.

However, in order to ensure the absorption in the more frangible areas at the limit of the ultraviolet, where the eye can only provide uncertain observation, photographs of the absorption spectrum were made by means of a spectrograph. The results are presented in the same manner in the form of absorption curves on Table XIII, FIGS. 1-9. The upper curve in the individual figures relates to the absorption of the more concentrated, the lower to that of the more dilute lungs. It is noteworthy that all the nitro derivatives show a considerable absorption towards the more frangible part of the spectrum.

The absorption curve of pseudonitroanthragallol, FIG. 3, in alcoholic lung showed two absorption maxima in opposite, lower lung, one next to D in yellowish green, a second in blue.

The absorption spectrum of  $\beta$ -nitroanthragallol, Fig. 5, in aqueous lung with little caustic potash is remarkable. The purely emerald-green lung shows a delicate, even absorption from red to yellow, on the other hand from blue-green to ultraviolet, so that a rather narrowly delimited emerald-green band in the spectrum around .notes, \_ar, i\_st; . with stronger ver

• - .,.,, K\_ •' . '•••,

However, permeability occurs in the orange-red. ix.-Nitroanthragallol, Fig. 7, gel in alcohol, shows, with greater dilution, an abruptly rising absorption curve against violet.

Most striking, however, are the absorption spectra of the amido products, Fig. 8, which show three absorption stripes, in yellow, green and light blue, but, as is often the case with such dyes, flow together in a closed band when the concentration is higher; the amido products which are obtained from 7- and  $\beta$ -nitroanthragallol, as well as that obtained from the greasy mother liquor of  $\beta$ -nitroanthragallol, show the three absorption strips mentioned in exactly the same place, as has been ascertained by multiple experiments on these absorption strips, but it appears

the relative strength of these three stripes may not be exactly the same in all cases, although they are is very similar.

34

J. M. Eder and E. V a l e n t a, Absorptionsspectra der Nitro- und Amidokper.

The aqueous lung of ~-amidoanthragallol, Fig. 9, also shows separate absorption stripes, but not as clearly as could be observed in the alcoholic lung; on the contrary, two absorption stripes appear only with greater dilution, in green and blue-green, which are a different position in the spectrum than is the case when using an alcoholic lung. In the alcoholic lung the whole absorption is shifted further towards the red side of the spectrum, while in the aqueous lung it lies somewhat further towards the more breakable end of the spectrum.

Similarly, the absorption band of the lung of (: i-nitroanthragallol in concentrated sulfuric acid, Fig. 6, is shifted further towards Roth than the absorption band of the alcoholic lung, without, however, noticing a significant change in the appearance of the absorption strips in freshly prepared lung. That would be what rigens, just like the absorption spectra not specifically discussed here, emerges directly from the graphical representation given in FIGS. 1 to 9.

Government Councilor Prof. v. Perg he had the ability to examine the coloring power of the nitro and amido compounds, and he informed us that these dyes behave like the other alizarin dyes, that is, they form colored metal lacquers. The colors produced by the nitro compounds on calico, which is preprinted with aluminum and iron stains, are light brown.

The colors of the three nitro compounds cannot be essentially distinguished from one another; (: i- Nitroanthragallol shows the relatively most intense, pseudonitroanthragallol the weakest color with the same quantitative coloration.

The two amido products give the aluminum-stained goods a reddish-purple color, namely ~-amido ~-anthragallol more intensely than the ~-amido product. Iron stains turn gray-violet.

The samples at 60 ° C. proved to be genuine against soap (oil lung from Marseilles soap).

The amido derivative and the nitro compounds were dyed on stained wool, for which purpose sheep's wool with potassium dichromate and whiteinstein, aluminum sulfate and tartar, iron sulfate; Aluminum sulfate and tartar were pickled in a known manner. The so prepared Eiteten and washed fabrics were dyed with 6% dye each (based on the weight of the goods).

Aluminum paints chrome paints iron-aluminum paints

~ -Amido derivative stains. violet violet dark purple brown

~ -Nitroanthragallol colors dark brown dark green brown dark brown

The colors of the amido derivative are characterized by the violet shade, which is significantly changed to brown-violet by iron compounds. The color intensity is important, as is the wash and soap fastness.

Using the process of making Tkischroth, the amido derivative gave violet, soap-fast colorations, which also demonstrated the usefulness of the dye in this direction.

Plate XIII.

Nitro compounds of

anthragallol. Aa BO G HK

Fig. 1. Pseudonitroanthragallol in aqueous lung.

111112tf? 1 iF

Fig. 2. Pseudonitroanthragallol in aqueous potassium hydroxide solution. IIII I Ivi =

11 Fig. 3. Pseudonitroanthragallol in alcohol.

IIIIk! J EiF

Fig. 4.  $\beta$ -Nitroanthragallol in alcohol. IIII 111? 1 II

Fig. 5.  $\beta$ -Nitroanthragallol in aqueous potassium hydroxide solution. It [] Lf = I II

Fig. 6.  $\beta$ -Nitroanthragallol in concentrated sulfuric acid.

111112: 1 1 II

Figure 7.  $\alpha$ -Nitroanthragallol in alcohol. 1111 \ Jd =? F II

Fig. 8. c,; - and  $\beta$ -amidoanthragallol in alcohol.

IIII Litti [

Fig. 9.  $\beta$ -Amidoanthragallol in aqueous lung. 1111 Lbl: 1 E.

Pressure of the k. k. Graphic teaching and research institute in Vienna.



# The line spectrum of silicon.

J. M. Eder and E. Valenta.

(Presented at the meeting of the Imperial Academy of Sciences on January 13, 1898.)

In a previous paper we have dealt with the study of the wavelengths of the lines in the emission spectrum of silicon from violet to the extreme ultraviolet. At that time we used a quartz spectrograph with a prism to record the spectra in question, and therefore obtained spectra which naturally showed a relatively small dispersion in the less frangible part. Since we had meanwhile set up a large grating spectrograph, we set about revising the results previously obtained with the quartz spectrograph.

In the meantime, a number of excellent "standards" had been published by Rowland, which we used in this work as a guide spectrum in conjunction with the iron lines measured by Kayser and the copper lines determined by us; this enabled us to determine the wavelengths of the silicon lines with the greatest possible accuracy. First of all, we generated from the coincidence of the main silicon lines occurring in the arc, measured from Rowland, with those occurring in the spark spectrum. However, we could not find Rowland's line,  $\lambda = 2263 \cdot 507$  in the spark spectrum of silicon, on the other hand we noted the presence of the main line  $A = 2542$  (more correctly  $A = 2541 \cdot 89$ ), as well as a number of broadened violet ones and faint ultraviolet lines. Some very faint lines of the silicon spectrum could, however, be obtained only with the quartz apparatus, but not with the grating, which is explained by the far greater luminous intensity of the former apparatus.

An alloy of silicon and copper and an alloy of magnesium and silicon served us to produce the silicon spectrum. With these alloys, which were used as electrodes, we obtained the same lines using a strong spark from a bottle as when using carbon or zinc electrodes, onto which silicon chloride is dripped while the spark is jumping over. The same results were obtained when electrodes made of elemental silicon were used. We emphasize again that the characteristic groups of lines, which are characterized by great sharpness, lie in the extreme ultraviolet, so that an identification of silicon by spectroscopic means can easily be carried out by means of the quartz spectrograph, but is difficult with a glass spectrograph.

1) cf. p. 75 of these treatises. 34 \*

J. M. Eder and E. Valenta, The line spectrum of silicon.

The following table contains the results of our more recent measurements, based on Rowland's normal lines. The same extend from  $\lambda = 4431$  to the extreme ultraviolet.

Eder Valenta Intensity ' ) Eder Valenta 1 Intensity 11 Eder Valenta 1 1 Intensity

4131 · 0 4128 · 2 3905 · 80 3862 · 75 3856 · 20 3854 · 00 3834 · 4 3826 · 7 3795 · 9 3791 · 1  
3191 · 1 3086

· 8 2987 · 77 2881 · 70 2689 · 8 4 4 3 3 3 1 1 1 2 1 1 1 4 10 1 widened)) widened widened,  
indistinct main

line 2677 · 4 2673 · 3 2659 · 0 2631 · 39 2568 · 8 2541 · 89 2534 · 7 2533 · 2 2528 · 60 2524 · 21  
2519 · 30

2516 21 2514 42 2506 99 2479 8 1 1 1 8 2 8 1 4 8 8 8 10 7 8 1 main line main line particularly

characteristic line group J 2452 22 2446 0 2443 46 2438 86 2435 25 2356 9 2303 · 3 2219 · 5  
 2218 · 15  
 2216 · 76 2211 · 8 2210 · 9 2208 · 1 2122 · 8 1929 · 0 33 2 2 8 1 1 1 1 4 3 3 3 2 1 main line}  
 clm,> rt, ri  
 stisoh, line group main line

1) In this table, the strongest lines are marked with 10, the weakest with 1.

The spectra of  
 sulfur.

Of

J. M. Eder and E. Valenta.

(Presented at the "meeting of the Imperial Academy of Sciences" on March 3, 1898.)

In spite of the many older works on this subject, the sulfur spectrum is practically unknown in its details. It is one of the most complex spectra. The line spectrum of sulfur shows numerous main lines which enable the detection of sulfur in vapors as soon as their position has been determined with sufficient accuracy, which has not been the case up to now. On the other hand, the band spectrum shows such an abundance of closely spaced lines that these "bands" cannot be resolved at all in the prismatic spectrum and even in the spectrum photograms, which we use our previously described grating spectrograph with short focus, which is a very good definition the many thousands of lines of sulfur appear so densely packed together in the individual parts of the spectrum, see Plate XVI, Fig. 1, that we renounced the attempt to run out the spectrum analysis of the sulfur with them.

We interrupted this work, which had begun several years ago, and only resumed it when we were in possession of a large Rowland's concave grille from Breas in Alleghany, which was one of a dozen such grids from Professor Rowland had been chosen by himself. This grid is of excellent performance, it has a radius of curvature of 15 English feet (4 m 59 cm) and contains 13000 lines in English inches. The definition of this grid is an excellent one and it should be noted that it is completely free of so-called "ghosts" is what appearances on the spectrum photograms can often be quite unpleasant. Both the spectrum of the first and that of the second order are of great brightness; the measurements described below were carried out on the second-order spectrum, and heliographic images of the spectrum photographs we have made are also included in this paper.

The adjustment of the apparatus was carried out with great care, the mounting of the grille is the same as we described it at the time when we discussed our small grille apparatus in these papers 1). The list was completed a year ago and we were able to proceed to the investigation described here, which was associated with difficulties. These were mainly necessary, the sulfur spectrum for about an hour at constant temperature and luminosity

1) cf. p. 161 of these treatises.

to expose by virtue of the Rren. In order to do this, the distillation of the sulfur in the vacuum tube, while the spark is breaking through, must be conducted in such a way that the part of the tube opposite

the gap does not become fogged with sulfur. A lot of people perish before the attempt is finished, so that the production of a good recording requires a lot of time, patience and me.

We measured several thousand lines, namely the line spectrum on two to four spectrum photographs in each area, the band spectrum, however, only with a single reading, whereby here and there smaller zones were measured twice for the sake of control.

The measurements were carried out by means of the measuring apparatus; We avoided using the projection apparatus to measure the lines.

We thus succeeded in measuring the spectra of sulfur in the pure state completely, the older work only proving in part to agree with our measurements, while we could not confirm other, earlier statements, as we shall find out more closely.

The emergence of the line spectrum in sulfur vapor was observed first [M. Seguin 1). The same vaporized sulfur in a hydrogen atmosphere and caused the spark to strike through the gas mixture. He observed a line spectrum with one red, three strong green, one blue-green, two blue and two violet lines, which appear cannulated towards the more breakable end. He also observed the three main lines when the spark struck through hydrogen sulfide and sulfur dioxide.

The existence of two different spectra of sulfur was discovered by Plücker and Hittorf 2); They described the spectrum of the first and second order (bands and line spectrum) of sulfur in their treatise "On the spectra of ignited gases and vapors" and mentioned that these spectra are most fully developed in vacuum under the influence of the discharge of fame Inductoriums arise without Leydener bottles (spectrum of the first order), or with Leydener bottle (second order spectrum). In the visible part of the band spectrum they observed 37 bands, 7 of which were in red to yellow (up to the Fraunhofer line D), 18 between yellow and blue (H3), 11 between blue and violet, and one in violet. When the tube is heated more strongly, lines of the spectrum of the second order are mixed in, but this itself only comes out pure when the Leydener bottles are switched on.

When the tube is moderately heated, the line spectrum is clearly discernible only in the yellow, green, and blue parts. On more intense heating, however, the brightness of the tube increases, and the red, orange-yellow, and the lines in the violet part of the spectrum emerge brightly. This spectrum, as well as the second sulfur spectrum, are shown in Plücker's and Hittorf's drawings in Plate XIV, FIGS. 4 and 5.

The general sight of the two sulfur spectra, as we made ourselves through observations with a small spectroscope (2 to 3 prisms), is very well reproduced by these figures, although the band spectrum is in reality much more complex than one seen in these and other older ones. Would suspect information.

J. Angström also occasionally occupied himself with a controversy with Wlner concerning the "third spectrum of hydrogen" with the spectrum of sulfur, which he was of the opinion that it might appear as an impurity in the hydrogen spectrum. He therefore made wavelength measurements in the line spectrum, but in view of the prism spectral apparatus he used, despite all the care he had taken, these were very imperfect, so that his information on the wavelengths did not appear to be precise. This is shown by a comparison with the measurements given below, which clearly show that, for example, the line groups measured by us) = 5647, 5645, 5640 · 5

1) Note sur les specters du phosphore et du soufre (Compt. Rend., 1861, vol. LIII, pag. 1272).

2) philosopher. Transact., 1864, vol.

CLV. The spectra of sulfur.

and 5640 \* 2 for Angström 1) are drawn as a single line ( $\lambda = 5645$ ), furthermore the lines 5616 and 5606 for Angström appear as a single line ( $\lambda = 5613$ ) the characteristic main double lines  $\lambda = 5433$  and  $5428$  as a single line ( $\lambda = 5432$ ) etc.

The observation he made about the influence of a strong magnet on the gas spectrum when the Rre was between the poles is very interesting.

He found that the  $\frac{1}{2}$  'hydrogen (from sulfuric acid) obtained by electrolysis gave the two Plücker's hydrogen spectra, but that when the tube was between the poles of a magnet, the sulfur lines emerged. The fecal hydrogen spectrum also changes with this treatment of the men, as he observed, and the hydrogen spectrum recedes.

A. Third 2) caused the bottle spark to strike through vapors of chlorinated sulfur and observed a spectrum of bands which he also obtained with chlorine selenium, etc. and which he ascribed to chlorine, while in addition to this spectrum the lines of sulfur and selenium that he did not measure and tellurium occur.

As a result, G. Salet worked in

several Fig. 34.

More recent treatises with the spectrum of bands and lines of sulfur, as well as they appeared in Plücker's rings and in the spectrum of flames of burning sulfur under certain conditions. He also gives schematic drawings of the spectra he has observed, which we reproduce exactly in Figs. 1, 2 and 3 of Plate XIV.

Salet describes in his first treatise 3) two spectra of sulfur, namely 1. a line spectrum that arises in the strong bottle spark and 2. a band spectrum that arises in the case of electrical discharges of low tension and also in the flame of sulfur burning in hydrogen's forms; it also appears less sharply in the absorption spectrum of the sulfur vapor. Said enclosed the sulfur in a tube without metal electrodes (Fig. 34), which had metal sleeves at the ends of the tube in place of such electrodes reaching into the interior of the tube. He heated with a lamp in order to make the sulfur evaporate and connected the brass sleeves between the poles of a Holtz'schen influenza machine. The Rre glowed as intensely as if it had been provided with electrodes going inside.

Salet poured a good deal of sulfur into the bar, distilled it off and in this way displaced air and foreign gases so completely that no more sparks could break through the melted and cooled bar. He found the following wavelengths:  $\lambda = 590$ ,  $\lambda = 564$   $\lambda = 544$   $\lambda = 522$  (strong) i.  $\lambda = 498$   $\lambda = 479$   $\lambda = 462$   $\lambda = 434$  · 5

581 560 538 515 492 475 453 5 431 5 577 554 532 508 5 487 5 470 448 (strong) 418 570 548 (strong)

526 (strong) 504 5 483 467 445 406

1) Compt. rend., 1871, vol. LXXIII, pag. 372. ') Compt. rend., 1871, vol. LXXIII. pag. 622. ') Compt. rend., 1871, Vol. LXXIII. p. 559.

J. M. Eder and E. Valen ta.

The spectrum of the sulfur burning in the hydrogen produced salt in such a way that it ignited hydrogen, which contains a small amount of sulfur dioxide, and directed the flame against a vertically falling layer of water (see later), whereby it was cooled and gave a nice spectrum, which is somewhat similar to the previous one. The wavelengths measured by Salet for the flame spectrum were:

). = 550). = 483). = 453 x 5

515 479 448 408 5

509 476 4-! 4 5 (strong) 404

504 475 (strong) 438 5 396

498 (strong) 467 431 5 (strong)

492 (strong) 462 429 (strong)

487 · 5 457 · 5 (stack) 419 furthermore Salet f gives the absorption spectrum of sulfur the bands  $\lambda = 471, 465, 462, 456, 445$  and 437. In later treatises Salet repeatedly referred to the spectrum of sulfur (1) and gave the first detailed report of his measurements of the line and band spectrum of sulfur in his dissertation<sup>2</sup>). Locky er 3) also received the cannulated absorption spectrum of sulfur vapor described by Salet.

Gasse-Iberg<sup>4</sup>) also measured the lines of the sulfur spectrum, which he created when used'

observed of certain types of glass in strongly evacuated tubes, whereby the glass becomes sulfur- containing and when a powerful spark struck it gave a (albeit impure) sulfur spectrum (line spectrum). A comparison of this sulfur spectrum with that of Pickers and Hittorf shows that the latter is more linear, soprobably at a lower temperature. greater pressure and stronger spark.

According to Ci am i c i an <sup>5</sup>), the line spectrum of the sulfur should not experience any broadening in this print, but the lines should remain completely sharp, an indication which we have to contradict on the basis of our observations, which will be explained in more detail in this treatise.

A. de Gram o n t describes in a treatise the spark spectra of some minerals (sulphides) the spectral phenomena which conductive minerals (lead luster, pyrite, calcopyrite, zinc blende, realgar etc.) switched between the electrodes of an inductor, gave <sup>6</sup>). In addition to the main lines of the metals, which are characteristic of the minerals, he always received sulfur spectra, which appeared more completely and intensely than the spectra of the metals themselves. He used this method for spectroscopic mineral analysis in the visible part of the spectrum.

Own attempts.

At first we tried to use the test arrangement Salet's (see pag. 271, Fig. 34) for the production of the sulfur spectrum. However, the success did not correspond to our expectations, because the heating was uneven, the vapor pressure inside the tube was also variable as a result and the lines of the spectrum changed as a result during a spectrum recording

1) Inden Camp. rend., 1872, vol. LXXIV, pag. 865, Salet remarks with regard to a treatise by Gerner "On the absorption spectrum of sulfur vapor" that he (Salet) had already described this earlier.

2) George Salet: "Theses presentees a la faculte des Sciences Paris sur les specters metalloides", 1872. 3) Lockyer sur les spectres des vapeurs aux temperatures elevees. Camp. Rend., 1874, vol. LXXVIII, pag. 1790.

4) Bull. de l'academie de St. Petersburg, 1880, Vol. II, pag. 307; Kayser: "Spectralanalysis", 1883, pag.

320. Ames later made the analogous remark regarding the occurrence of the sulfur spectrum in Pickers.

5) meeting area d. kais. acad. d. Wissensch., Vienna, mathem. -natural Cl., Vol. LXXVIII, 1878.

6) Camp. rend., May 1894, I. Semester, Vol. CXVIII, No. 11, p. 591; also Camp. rend., 1896, June 8. Drawings of Spectra of Sulfur.

(Photozinkotype and collotype based on the original drawings Salet's, Pickers and Hittorf's.)

700 "650 600 SSo Sooj,!) Oioo

Fig. 3. [111 111, 1,11111,1, 11,11111111111111111 ~  $\beta$ 1ii / 111i ,,, ~, r' ~ r1,1, ~, ~, ~, 11111 ~ 11 ~  
,, ~ 1 ~, ~ 1 1,1 ~ 1 ,, ~, ~, 1t1, ~ 1 ~, 1 ,,, ~ ~ ,,, 1 ~ 11 ~ 1111

1

ln111111111111111 H 111rm1111 1111111r1 1m 11 1 1 rr 1 1 1, r 1, 1 wr rri 111Tp1111

11 20 3 26 3 2 3- :, 10 3o bo 6.o 70 80 90, oo no l> O 130 140 160

•

Fig. 4.

Well Hats Hy

Fig. 1. Line spectrum of sulfur (after G. Salet). -Fig. 2. Band spectrum of sulfur (after G. Salet).  
-Fig. 3. Flame spectrum of sulfur (after G. Salet). -Fig. 4. Line spectrum of the Sch ~ efels  
(after J. P 1 c k e r and  
J. W. H i t t o r f). Fig. 5. Band spectrum of sulfur (after J. P 1 c k e r and J. W. H i t t o r f).

..

their brightness became broader, narrower, etc. With this arrangement we were therefore unable to follow the spectral phenomena that occurred.

After several attempts we found that Rren with fused platinum electrodes (since aluminum electrodes melt easily) gave the best results. The shape of the men we used was similar to that which we wore e benzen for the production of the various mercury spectra at the time 1).

The tubes were charged with sulfur in the enlarged pear-shaped part of the tube, evacuated, and heated with the air pump until the sulfur began to distill, whereupon they were melted off. The vacuum tubes produced in this way were found to be completely free of air, hydrogen, hydrocarbons, etc., and the vacuum of the same at ordinary temperature is such that the spark does not break through.

The heating of the tubes, which is necessary to achieve a sulfur spectrum, was carried out in an air bath specially constructed for this purpose, which had an aluminum window placed in the longitudinal axis of the tube perpendicular to this, whereby the observation of the light in the capillary was possible without a locale Decay of the heated sulfur pipe could occur. As soon as the sulfur has a temperature of 60 to 70

° C, there is enough sulfur vapor. The spark strikes through the tube and the capillary tube glows bluish- white. The brightness is moderate and, as soon as no bottle spark is used, the band spectrum of sulfur arises.

With further warming the brightness of the capillary tube becomes much greater; it grows as the color of the light becomes whiter, until at last the capillary shines in a dazzling white light. The most favorable temperature is 100 to 150 ° C .; but the tube can be heated to 200 ° C. and the same band spectrum still occurs without the innumerable fine lines of it being broadened; At a higher temperature, a continuous spectrum seems to be added, and some lines which concern the line spectrum, the band spectrum oei, and there arise ice spectra, are mixed.

The exposure time for recording such band spectra of the sulfur was 5 minutes to 2 hours, depending on the brightness of the capillary light.

The line spectrum of the sulfur.

The spectrum of bands of sulfur appearing in Plckers' rings immediately changes into the spectrum of lines when the secondary voltage of the inductor is connected with one or two large Leydener bottles. This change can be seen clearly even with a pocket spectroscope, and the counter-production of the original drawings by Pecker Hit (see Facsimile Reproduction, Plates XIV, Figs. 4 and 5) does indeed give a clear picture of it , but does not allow any details to be identified.

We photographed the line spectrum at different temperatures, respective vapor pressure 2), and in this way, using our large concave grating, we were able to follow the stages of development of this spectrum exactly.

According to our experiments, the most favorable temperature for the creation of a sharp line spectrum is 100 to 140 ° C. If the temperature is too low, i.e. very low vapor pressures and a weaker bottle spark is used, the line spectrum is always added to the band spectrum.

1) cf. pag. 128 of these treatises.

2) In this series of tests, there was always sufficient sulfur in the pipe, so that the respective temperature

set the appropriate steam pressure. 35

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When the pipe is heated in an air bath to about 100 to 110 °, the line spectrum is formed with fairly great sharpness and the lines show hardly any verifiable broadening phenomena. Likewise, the lines become sharp if a distillation is initiated in the pipe by slowly heating one end, in which the sulfur is located, until the bottle spark breaks through and the other end becomes cold, so that the sulfur vapor condenses there. Even if there is only a little sulfur in the pipe (minimal traces) and this is heated more strongly, there is no broadening of the lines of the sulfur spectrum. With more intense heating of the vacuum (160 to 200 °) charged with excess sulfur, i.e. correspondingly increased vapor pressure, the color of the light in the capillary becomes whiter and brighter, but without reaching the brightness of the light phenomenon that occurs without a Leydener bottle. In the ultraviolet, the number of lines and their intensity increases; Strangely many lines broaden, partly on one side, partly on both sides, while others remain perfectly sharp. Many of the at 100 ° C; The main lines appearing are very strongly broadened towards 200 °, but remain very bright and are therefore even more conspicuous and seemingly more prominent for ocular observation. At 180 to 200 ° C. numerous new lines appear, partly as sharp, partly as blurred types. However, one must in no way believe that all sulfur lines become evenly lighter at higher temperatures; in some cases lines are at 100 ° C. brighter than at 200 ° C, while others are more intense, so that the appearance of the Liniengruppen is noticeable. We observed, however, that the gradual receding of certain sulfur lines with increasing temperature is intimately connected with rapidly progressing broadening phenomena, because the broadened lines become broad shadows and are then beyond observation. At a temperature of 220 ° C. it is difficult to send the bottle spark through the tubes filled with sulfur vapor, because the internal resistance of the tubes is already too great. At this temperature the symptoms of widening appear very developed. The spark becomes thinner, threadlike and ramified at the bottom at higher temperatures. In our sulfur rings, made entirely of glass, we could only observe the effects up to), > 3200; However, the glass is still permeable to light of shorter wavelength; If the sulfur spectrum no longer had a strong effect on the photographic plate there, the reason may be that it either becomes less light there, or, more likely, that the sulfur vapors have an excessively strong absorbing effect on the ultraviolet rays and therefore their exit from the pipe. Characteristic, conspicuous groups of lines in the line spectrum of the sulfur are the single line in light blue -! 716, the closely spaced lines 4549 and 4552 in indigo blue, the main lines 4464 and the line group 4285, 4282, 4278, 4269, 4267 9, 4267 2, 4253; but especially the most outstanding group in the photographic spectrum, the violet group 4189, 4174, 4162, 4153, 4145, 4142, then the double line 1,1 4028 9 and 4032 9 and finally at the beginning of the ultraviolet the main groups A = 3933, 3932, 3928, 3923. These groups of main lines in blue and violet have been demonstrable for all pressure conditions which we have included in the scope of our investigations, but with variable widening phenomena in the sense of our above examinations. Plate XVI, Fig. 3a, shows a part of this



area, namely at the border of the beginning strong widening; the lines of the iron-spark spectrum photographed next to it give at the same time a measure of the size of this broadening, while plate XVI, Fig. 2a, shows another area of the same spectrum with sharp lines (with lower vapor pressure) for comparison. To get a very clear picture of sulfur

1) Spectrum photographs of the iron spark on our table are partly photographed without a glass filter and then naturally contain "lines of the second order" as well as those of the third order, because we wanted to achieve a denser network of normal lines; the sulfur spectra, however, are pure spectra of the second order which the third order is filtered off.

Spectrums in its various widenings is shown in Plate XVI, Fig. 1a, the line spectrum of sulfur is placed next to the band spectrum at low temperature and the argon spectrum 1) distinguished by its sharp lines is photographed next to it. This shows that the line spectrum of sulfur can be obtained with almost the same sharpness as the argon spectrum, although individual sulfur lines on this table already show a tendency to broaden. The three spectra were taken with our small grating spectrograph to give a clearer picture. Plate XVI, Fig. 2, shows the lithium spectrum also in the stage of good sharpness, Fig. 3, on the other hand, shows another area in a state of fairly strong widening and Fig. 4, Plate XVI, the ultraviolet area in a state in which one part the lines are still sharp, another one has already changed.

The accompanying spectrum tables contain images of the green, blue, and violet parts, as well as the beginning of the ultraviolet of the line spectrum of sulfur. These parts, however, do not adjoin one another completely; rather, the individual spectral figures are missing small pieces, but the lines are measured by us from other spectrum photographs and given in the tables of the wavelengths: Other sulfur lines, which better withstand the broadening with increasing pressure, are  $\lambda = 4464, 4361, 4353, 4340, 4285, 4253, 3993, 3986, 3983, 3961$ , while numerous strong lines are subject to rapid spreading phenomena. At the same time we observed that sharp double lines unite to form a fuzzy main line; On the basis of our recordings, this gave us the impression that a new single line had emerged and that the bands of two independently existing lines had not flowed into one another. We therefore want to describe these as yet little studied phenomena in more detail and explain them using the heliographic images (Plate XVI).

Lines 4285 and 4253 widen only slightly with increasing pressure and remain in the earlier intensity ratio; 4267  $\times$  9, which had the intensity 4 at low pressure is greatly broadened and its intensity becomes = 8; at  $\lambda = 4267 \cdot 2$  the intensity at low pressure = 5, at higher pressure a strong broadening occurs, the line becomes faint and blurs with the line  $\lambda = 4267 \cdot 9$ , so that when viewed superficially it gives the impression of a single line broadened towards violet. Such conditions often explain anomalies due to the one-sided broadening of the spectral lines. The sharp double line at low pressure at  $\lambda = 4485$  disappears completely with stronger prints and makes room for a widened single line, but it gives the impression that a new independent line has emerged, as we could no longer find any edges or remnants of the previous double line. The line 4483  $\cdot$  6 next to it also widens, but gets apparently symmetrical band-shaped shadows on the left and right, which at  $\lambda = 4483$  and 4482  $\cdot$  8 and are undoubtedly independent lines (but certainly not "ghosts"). The line  $\lambda = 4525 \cdot 1$  has a sharp line to the companion  $\lambda = 4524 \cdot 8$ , which disappears completely with increasing pressure, etc. Thus, with increasing vapor

pressure in the pipe, the intermolecular movement created under the influence of the bottle spark was influenced;

1

this manifests itself above all in strong widening phenomena, but also, as we have shown, in the disappearance and reappearance of lines; but the predominant number of lines remains in the old position, so that one can safely explain the line spectrum of sulfur as characterized.

The observations made are therefore not so much of interest for the identification of sulfur in gas mixtures as for the precise knowledge of the internal molecular motion in spectral phenomena. Our tables of wavelengths refer to the sharp one, respectively

1) The same thing is abundantly exposed and, since it was taken with the grid from a short focus, shows in places the appearance of the so-called "ghosts."

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The spectrum is fairly sharp before the appearance of the broadening phenomena, because only in this way can sharp information on the wavelengths be obtained, on the basis of which the broadened lines can be identified without any difficulty.

Shift of spectral lines in the sulfur spectrum with changed pressure.

We have occasionally shown our investigations first of all in the argon spectrum 1) that in P 1 cke rian at constant pressure changes in the wavelengths of certain groups of lines undoubtedly occur only through a change in the form of electrical excitation, which changes by shifting the lines by an easily measurable amount express.

No other analogous phenomena in Plker's were known since then. In our investigations we have endeavored to find the conditions for the sulfur spectrum under which analogous shifts can be forced, and we succeeded in doing this by increasing the vapor pressure in the sulfur tube. If the spark of a Ruhmkorff inductor, amplified by 2 to 3 large Leydener bottles, strikes through the sulfur tube at low vapor pressure, then very sharp line spectra arise, while with gradually increasing vapor pressure widening, initially of some groups of lines, occurs and with further increased pressure the widening of the number in question of lines of the sulfur spectrum enter, while a smaller number, though not quite sharp, remain only moderately broadened.

With many of those strongly broadened lines there is a change in wavelength; The lines are shifted towards Roth, and indeed they suffer a shift of an average of  $0 \cdot 5$  AU. We have photographically fixed this shift phenomenon, which is most remarkable, and bring some of these photographs in enlargement to Plate XV, Fig. 1, as ours Otherwise the information might lead to doubts. Two sulfur spectra (line spectra) have been photographed there for coincidence, one with sharp lines when the pressure is low, the other with broadened lines when the pressure is high. It can be seen from this that individual lines,

for example  $\lambda = 4285, 4253$ , under these conditions did not suffer any shift (change in wavelength), while the lines  $\lambda = 4294, 4281, 4283, 4278, 4269, 4267 \cdot 9, 4267 \cdot 2, 4259, 4257, 4231, 4217$  etc., have suffered a very clear shift of about 0.5 AU against Roth (see Fig. 1b of the heliographic Plate XV after photographic enlargements of the original spectrum recordings).

The picture shows this so clearly that any doubt can be excluded. It can also be seen from the figure that several previously barely visible sulfur lines, even if they have become blurred, result in greater brightness have formed.

We attach great importance to the partial occurrence of the shift phenomena in the spectrum, and believe that those groups of lines which accept the enlargement of the wavelengths in question more easily than others which are difficult or impossible to deal with, play a special role in intermolecular movement of the vapors of sulfur and perhaps indicate the existence of more permanent and less permanent components of it.

#### Band spectrum of sulfur.

As has been mentioned, the band spectrum of sulfur gives the impression of a spectrum consisting of bands with different maxima if the dispersion is smaller. A good over

1) Memoranda d. mathem. natural Cl. d. kais. acad. d. Wissensch., Vienna, 1896, Vol. LXIV.

If he sees the habitus of this spectrum with moderate dispersion, it gives us the photographic reproduction of this spectrum contained in Fig. 1, Plate XVI after a picture with our small concave grating. The swell line spectrum is shown next to it, whereby at first glance it becomes apparent that the two lines not only have no similarity with one another, but do not even have common groups of lines.

The argon spectrum shown in Fig. 1c of the same table is used for orientation. Fig. 5, Plate XVI shows part of the band spectrum after a photograph of the second order spectrum, which was taken with our large concave grating, namely the area from  $\lambda = 4720$  to  $\lambda = 3940$ . The same gives the details in the complex structure of this spectrum very good again. The structure can be seen even more clearly from the enlargement of this spectrum, as shown in Fig. 3, Plate XVI.

In order to establish the relationships between our measurements and the old data (see above), we tried to estimate the position of the maxima in the band spectrum approximately and give the counter-creation of these numbers against those of Salet. From this compilation it can be seen that the spectrum we examined is really identical to that observed by Salet.

Eder -Valenta 1 Salet II Eder -Valenta 1 Salet II Eder -Valenta 1 Salet Eder -

Valenta 1 Salet 5596 5594 5191 5192 4843 4842 4532 4521

5534 5475 5529 5470 5146 5093 5144 5089 4794 4748 4787 4746 4498 4481 4480

5419 5416 5040 5037 4710 4706 "4434 4435

5359 5354 5000 4990 4663 4651 4376 -

5310 5310 4936 4936 4610 4607 4359 4355

5253 5248 4893 4895 4565 4562

In order to finally determine the band spectrum of sulfur, at least in the photographically active areas, we made it from light blue to ultraviolet ( $\lambda = 3600$ ) and determined the wavelengths of about 10,000 lines. The almost entirely extremely fine, sharp lines are so close to one another that it can be assumed that the entire extent of the band spectrum in the visible and invisible part is so densely packed that at a distance equal to the double sodium line, on average there are thirty lines; if one were to expose even longer, new lines would come out, and even when using an instrument with such good dispersion as our large grating spectrograph, the band would appear closed. In the band spectrum there are no shaded nebulae, but consistently clusters of sharp fine lines and no outstanding resting points or outstanding main lines can be found, as they are in other line-rich spectra, such as iron, platinum, cobalt, Nickel, easy to find. Swellings of the brightness of the spectrum band in numerous maxima are found, but these are less due to the strength of the lines than mostly to their great number in the same space. Precisely determinable edges, which impose a characteristic impression on other band spectra and allow easy identification, as for example in the band spectrum of nitrogen, mercury, water, ammonia, cyan etc., are missing here.

If, nevertheless, when observing the ocular with small spectroscopes, one believes that certain maxima can be expressed numerically in wavelengths, then this only reflects the subjective sensation; the readings are so variable, according to the observer, the apparatus, and the brightness of the spectra, that they are of little value.

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We tried to determine these maximums in the sulfur band spectrum with a Krs's spectral apparatus with a flint glass prism of  $60^\circ$ , as well as with a compound prism; On the other hand, we scaled down our spectrum photographs in order to compress the maximums into narrower, more easily identifiable strips, but the results were not very consistent. The ocular readings pretty much agreed with Salet's numerals; those obtained by the photographic process give only in the blue region incidental agreement (see above), in the violet both reading methods always diverged and in the ultraviolet the maxima became so confused that we refrained from reading them, but the heliographic image gives a true picture of the spectral phenomenon in question.

The question now arises whether the lines of the line spectrum of sulfur also occur in the band spectrum? This must be denied insofar as the main lines of the former spectrum by no means appear in any clearly noticeable manner in the latter; it may well be that among the many thousands of fine lines of the sulfur band spectrum there are lines of approximately the same length, perhaps also coincidences, but in any case these lines of the line spectrum then play such a subordinate role in the band spectrum, indeed they are hardly detectable, that one must designate both kinds of spectra of sulfur as independent characteristic types.

Flame spectrum.

The flame spectrum of sulfur is to be regarded as a band spectrum. It was first observed by M u 1 of 1) by connecting a glass tube to a hydrogen apparatus which was placed near the platinum-tipped MFig.

35. contained some sulfur. If this is heated and the hydrogen is ent

. A flame is obtained which has a blue core and supplies a band-like, weakly interrupted spectrum, in which three violet lines stand out, which are very broad, while the spectrum is still an innumerable number of green, blue and violet lines Lines shows ». The entry of hydrogen sulfide or carbon disulfide into the hydrogen flames has a similar effect (however, do not allow too much hydrogen sulfide to enter, otherwise the phenomenon becomes indistinct).

H. W. Vogel 2) obtained the band spectrum of sulfur when burning carbon disulfide when nitrogen oxide was blown into the flame. Salet studied the flame spectrum of the sulfur-containing burning hydrogen very carefully; he showed that the blue inner cone of the flame usually gives a continuous spectrum; the band-like spectrum only appears when the flame is greatly cooled by directing it against a sheet of platinum that has been chilled by trickling water (see Fig. 35).

In the flame spectrum of sulfur the red bands are which

in the spectrum of the sulfur bands in the Geissler tube are very bright, little or not developed, on the other hand the yellow, green, and then very strong, broad stripes in violet, which are clearly discernible in the case of low dispersion, appear sharply after the violet, running after the violet

1) M u 1 der: <About the spectrum of sulfur, phosphorus and selenium », Journ. pract. Chem., Vol. XCI, pag: 112.

2) V oge 1 experimented with the so-called Se 11e lamp, which supplies a very actinic light (see Eder: Ausfriges Handbuch der Photographie, 2nd ed., Vol. I, I. Abth., P. 532 ). He observed the canceled band spectrum and described this in the reports of the German Chemical Society, Vol. VII., Pag. 1522.

the red side of the spectrum; several broad purple stripes are particularly noticeable due to their brightness.

If a hydrogen flame is left to burn from the platinum tip of a normal incinerator tube after salt and it is directed against sulfuric acid, crystals of ammonium sulphate, sodium sulphate, alum, gypsum (but not barium sulphate), sulphites, hyposulphites and even glasses containing Glauber's salt, it turns bluish and gives the sulfur spectrum<sup>1</sup>). This can be used for the qualitative detection of sulfur, but the sample is not particularly characteristic. Salet gives a picture of the flame spectrum, compared with the band spectrum appearing in Geisler's Rren (Fig. 4 and 5, Plate XIV), which gives the general orientation, but does not suffice to answer question 2 suggested by Schuster) to decide whether the flame spectrum is a mixture of the band and a compound spectrum. We did not succeed in the decision of this question either because, despite our efforts, we could not produce the flame phenomena continuously and brightly enough to photograph the specirum by means of the large concave grating and because the results of the exposure with more powerful apparatuses of smaller dispersion to answer the question were not reach. But if we did not succeed in unraveling the details of the flame spectrum, then on the basis of the ocular observation we cannot ignore the view that this spectrum essentially agrees with the

band spectrum mentioned above and is therefore an imperfectly developed band spectrum of sulfur is to be understood.

Compound spectrum of sulfur.

C. Runge and F. Paschen investigated a real spectrum of sulfur, which is called the "compound spectrum" of oxygen (Wiedemann's "Annal. d. Phys. u. Chem.", 1897, Vol. LXI, pag. 642) is analogous.

Compound line spectrum of sulfur according to Runge and

Paschen. Wavelengths J I Wavelengths J II Wavelengths J I

7242 00 2 6046 23 6 5449 99 3

6757 40 7 6042 17 5 5444 "58 2

6749 06 6 5890 08 2 5381 19 4

6743 92 5 5883 74 2 5375 98 3

6538 82 1 5879 79 1 5372 82 2

6536 55 1 5706 44 8 5295 82 4

6415 68 4 5700 58 7 5290 89 4

6408 32 3 5697 02 6 5287 88 2

6403 · 70 '2 5614 · 48 5 5279 · 19 6

6396 90 1 5608 87 4 5279 81 5

6395 · 10 1 5605 · 52 3 5278 · 31 3

6176 01 1 5507 20 5 4696 49 6

6173 77 1 5501 78 4 4695 69 8

6052 97 7 5498 38 3 4694 36 10

According to Runge and Paschen, the compound spectrum (series spectrum) of sulfur arises in such a way that a vessel provided with platinum electrodes was provided with a flask-like end, into which container sulfuric acid was poured. The Rre stood with one

1) Repertory Brit. Assoc., 1880, p. 272; H. Kayser: "Spectralanalysis", 1883, p. 332.

2) Camp. rend., 1868; Poggend: Anna l. Phys. u. Chem., Vol. CXXXVII; H. W. Vogel: • Spectral analysis

», 1889, pag. 302. Hydrogen passed through sulfur ammonium gives a continuous spectrum when ignited, as does carbon disulfide mixed with hydrogen (after H. W. Vogel 1 a. A. O.).

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Apparatus for the electrolytic development of oxygen in connection. The sulfuric acid in the flask was heated to the boil until some steam had condensed in and in front of the capillary of the Geissler tube. If one waited until the water vapor, which had also been produced, had been absorbed again and during which oxygen was allowed to pass through the pipe, then immediately afterwards the series spectrum of sulfur appeared in the Geissler tube, next to it the compound spectrum of oxygen and after some time the hydrogen spectrum appeared. The main lines of the new sulfur spectrum appeared when sulfur was heated in a tube and oxygen was added, and also when sulfur dioxide was introduced. In both cases the band spectrum is of the essence, and it appears, Runge and Paschen add, that the new spectrum appears only in the presence of oxygen.

A conclusion regarding the nature of the Runge-Paschen compound spectra, whether or not they contain lines from the elementary spectrum of sulfur, was inadmissible before the end of our present work, because the sulfur spectrum was not guaranteed. On the basis of our work, however, we can now say with certainty that the spectra of elemental sulfur we have observed have nothing in common with the "compound spectrum" of sulfur and that the latter is in any case due to an oxygen compound in sulfur.

#### Spectrum of sulfides.

In order to investigate the role which sulfur (sulphide sulfur), which is associated with metals, plays in the spark spectrum in the air, we made rods of sulfur-silver, which conducted electricity well and gave off great sparks. In these, even with spectroscopes of smaller dispersion (especially in the aureole), the characteristic main lines of sulfur can be clearly perceived. In the ultraviolet, too, under these conditions the lines of the spark spectrum of sulfur are clearly obtained (in addition to the metal and air lines) and indeed quite sharp with moderate widening of the appearance of the air lines, which are less sharp. This spectrum is probably not exactly identical to the spectrum of sulfur in vacuum, but it essentially agrees with it.

Table I.

•

#### Line spectrum of the sulfur.

Eder and Valenta (Rowland units) Angstr Hasselberg Plker and Hittorf Salet

- - - - 6579 -

- - - - 6454 -

- - - - 6421 -

6400 6390 6325 6310 ---- Oil seen by us, but not determined more precisely 6404 6390 6321  
6309 6400 6390 6325 6310

6290 - J - - 6290 6290

- - - - 6152 -

- - - - 6111 -

- - - - 6009 -

- - - - 5866 -

5819 543 2 - - 5810 -

- - - - 5780 -

5665 123 4 5671 - 5667 5670

5662 741 1 blurred - - - -

5660 289 6 - 5659 7 5657 5660 1

5648 565 1 - - 5650 5655 'l.

Eder and Valenta (Ro wland units)

Angstrm Hasselb erg Pllicker and

Hittorf Salet

5647 296 5645 920 5640 535 5640 257 5616 844 5606 349 5579 327 5565 097 5559 129 5556  
141 5536

968 5526 458 5520 749 5518 968 5509 799 5478 589 5477 649 5475 209 5473 791 5468 565  
5454 000

5434-737 5432 994 5428 907 -5401 035 5345 832 5320 894 -5233 187 5230 040 5227 406 5227  
072

5220 872 5219 · 650 5212 · 803 5207 · 482 5201 · 520 5201 · 149 --5160 · 348 5142 · 512 ---  
5103 · 535

5098 · 890 5051 · 874 5047 · 499 5039 · 596 5032 · 657 5027 · 408 5014 · 248 5011 815 5009  
762 5007

010 4993 733 \ '>) J 8 2 4 8 4 8 6 8 1 4 3 5 3 3 10 2 1 2 8 1 10 2 10 9 --3 8 8 -1 1 1 1 1 3 8 2 2 6 -  
-2 3 -----4 1

1 3 2 8 48 3 6 1 3 blurred widened "blurred" "> 1)>) 1 5645 --- 5613 ----- 5474 -5451 -5432  
-----

5345 5322 - ----- 5207 -5191 ----- 5027 5013 --- 4994. ~>) II II --- 5639 3 -5603 -5561 3  
-----5516 9

5507 3 ---- 5470 5 5451 o -5438 1 5429 7 -5418 4 5386 6 5341 7 5319 2 ----- 5217 8 5214 4 --  
5200 1 ----

5142 5 --- 5102 9 5078 3 -5044 9 -5032 5 -5012 7 --4993 9)>))> 1 --- 5641 5618 5609 5584 5568  
-5558 5:

' : 32 -5522 5508 ---- 5473 5452 -5438 5425 --- 5338 -5304 5269 5231 --- 5218 -5207 -5199 5191  
5182 - ·

5143 5141 5140 5124 5110 5096 5068 5044 5036 5030 5024 5013 -5004 5003 5000 1 5647 ----  
5610 -

5570 ----- 5510 -5477 --- 5455 -5432 ---- 5350 5320 ----- 5220 5217 ---- 5205 - 5160 ----- 5103 ---  
5030

5024 5013 -5008 -5000



1) poor in light and widened; only detectable with quartz spectrograph.

If one compares the lines measured by us with the lines of the calcium spark spectrum found next to them by Exner and Hasch e k, the result is undoubtedly that the last-named researchers were looking at an imperfectly developed spark spectrum of calcium. We must also note that from this imperfectly

developed spectrum the lines'  $A = 4486 \cdot 1$  and  $2889 \cdot 67$ , frozen by Exner and Haschek, have to be deleted, since they do not appear in the spark spectrum of metallic calcium. We ought to have found these lines (if they were true calcium lines) simply because we could easily detect much weaker lines which no longer appeared in Exner and Haschek's calcium spectrum; on the other hand, in this spectral region there are other lines that are poor in light and difficult to detect, which only appear clearly when metallic calcium electrodes are used.

If one compares the spark spectrum of the metallic calcium with the calcium arc spectrum, the comparatively great correspondence of the two in the less frangible part is striking, in that there pretty much all the stronger lines of the spark appear as strong lines in the arc; Only in the more breakable ultraviolet does the spark spectrum, with several rather strong lines, show itself to be richer in lines, and noticeable differences appear.

Furthermore, it should be mentioned as a remarkable result that in the complete calcium spark spectrum among the lines broadened on one side according to Roth, those were also found several times which also occur in the 1m arc spectrum (Kayser and Runge) with exactly the same characteristics ( $A = 4098, 4095, 3487, 3474$ ); on the other hand, broadened lines occur in the calcium arc spectrum according to Roth, which appear sharp in the spark spectrum and vice versa.

On the basis of our observations, therefore, it is not practical to look for a difference between the arc and spark spectrum in that the lines in the spark spectrum according to Roth are blurred and appear sharp in the arc spectrum.

Rather, this broadening phenomenon of certain lines towards red, others towards violet, others over evenly on both sides is a general occurrence among the most diverse variations, which belongs not only to the calcium spark but also to the arc. Among the lines of the spark washed out against Roth,  $\lambda = 3737, 3706, 3181, 3179$  and  $3159$  are particularly striking. In these lines one also notices the eccentric inversion phenomenon, that is, the inversion phenomenon does not lie in the middle of a symmetrical thick line, but rather towards violet towards or with other advantages; the side of the non-inverted environment which is towards Roth is more widened and widened more intense than the other side.

This widening phenomenon against Roth, which gives the impression of a line shift, is mentioned by Exner and Haschek; they indicate that the reversed lines of the spark do not coincide with the same but not reversed lines of the spark 1), but that the latter are shifted by an average of 0.11 Angstr's units towards Roth, which they in the sense of the investigations Humphrey and Mohler's, Jewell's and others interpret them as a result of the greater vapor density or perhaps the locally increased pressure in the spark; They assume that in the strong crackling spark of the inductorium they are using, there is a large pressure difference (12 to 14 atmospheres) in the spark path.

Since we had independently discovered the phenomenon of the line shift in argon 2) and the sulfur spectrum 3), the phenomena described in the calcium spark interested us to a great extent, and we repeated the experiments. In fact, in our first experiments we obtained spectral photograms (first order) which appeared to confirm the shift phenomenon.

We generated a crackling spark as intense as possible between calcium electrodes with the help of a great Glory Korffian inductor with the switching in of a corresponding number of Leydener bottles and obtained precise results Reversal phenomena; In addition, we photographed the spectrum of the spark

between two coal tips impregnated with a little calcium salt and obtained the same lines not the other way around, but as noticeably broad, dense stripes, the center of which we measured and found an apparent shift towards Roth. However, we did not succeed in obtaining even approximately constant numbers of these displacements, but rather they fluctuated with one and the same spark with different photographs taken quickly one after the other and with differently strong, longer or shorter lasting development of the latent image. In a series of tests, for example, the variation was 0.024 to 0.055 fear r m 'see units, slightly more, and the type of development (hard or soft developer) and the plates themselves seemed to influence the result.

In order to be able to follow the phenomena with the greatest possible accuracy, we worked with the second and third order spectra, thus achieving a much larger list than that which our predecessors had used in studying these lines.

1) Exner and Haschek admit the coincidence of the inverted lines of the spark spectrum with the inverted lines of the arc.

2) cf. p. 216 of these treatises.

3) cf. p. 269 of these treatises. 43 \*

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The exposure time varied greatly in more than a dozen pictures and the silver bromide plates and developers were chosen in such a way that the gradation of the spectrum photos was as delicate as possible and the details of each individual broadened line were clearly visible.

We photographed not only the reversal phenomena in the one-sided broadened lines, but also in the other groups of lines that are sharp on both sides and give a true facsimile in the heliographic illustration of our Plate XVII. The spectrum photograms of the lines) = 3181, 3179 and 3159 come from the third order spectrum, those of the lines) = 4455, 4454, 4435 and 4425 from the second order spectrum and were obtained simultaneously on the same plate. For greater clarity, we have enlarged these photograms moderately (approx. 4 times), which was easily possible given the great sharpness of the images without significantly impairing them.

First we describe the normal reversal phenomena of uniformly sharp or symmetrically broadened lines, for example calcium A = 4454, 4435 · 1 (see Table XVII), because these phenomena are typical:

1.

A line that is evenly sharp or symmetrically broadened on both sides is exactly centrically reversed and the non-inverted line produced by an impurity or weak metal vapor co "incides completely with the reversal phenomenon, namely in sparks and arcs with one another, as our picture clearly shows.

2.

In the case of those lines which are broadened on one side or intensely sharp on one side, but blurred and gradually broadened on the other side, the reversal phenomena are generally different.

At first we observed that with such lines broadened towards Roth, for example the line  $\lambda = 3179$  and  $3159$  of the calcium spark spectrum (see Plate XVII), furthermore at  $\lambda = 3737$  and  $3706$ , the one-sided broadening does not take place in such a way that around the brightest part of the line (which can be established by a very short exposure) the indistinct, strong broadening phenomenon extends exclusively towards Roth. Rather, the sharp edge is likewise, but very slightly widened towards violet, so that it does not have a completely constant position, but rather is somewhat towards violet, and indeed the maximum of the brightness of such lines lies towards the violet side.

It is therefore extremely difficult to make a constant wavelength measurement on lines of this type that have been exposed for a longer period of time; only through a very short exposure and careful photographic elicitation can the wavelength of the dominant bright point of the line be determined with constant accuracy and it corresponds to the main oscillation of the spectral light phenomenon.

If one brings about the corresponding reversal phenomena in such lines by increasing the amount of steam, etc., these appear asymmetrical, as do the non-reversed lines; the eccentric shift to violet occurs, as described by Exner and Haschek in agreement with us.

An extensive series of experiments carried out by us in the third-order spark spectrum showed without a doubt that with very short exposure and careful elicitation the non-inverted line coincides with the inversion phenomenon; the finest lines of calcium show  $\lambda = 3181, 3179, 3159$  on our heliographic table XVII this coincidence 1).

The most intense, i.e. the dominant, the non-inverted line remains in the same place with longer exposure 2), next to it the enormous one-sided widening phenomenon is countered

1) The fine, non-inverted lines were produced by carbon electrodes which were deliberately contaminated with a little calcium salt, the inversion phenomenon obtained with calcium electrodes and the strongest bottle spark of a large Ruhmkorff inductor.

2) Apart from the slight increase towards violet.

Roth noticeable, which with vigorous development and use of "hard and vigorously working" plates converges with the original maximum to form an apparently uniform stripe (thick line); if one measures the middle, one obtains variable numbers: 1 values of a "shift towards Roth", or more correctly: 'a fuzzy broadening phenomenon towards Roth 1). The apparent center of the same fluctuates with the time of exposure and the type of development and one has not fixed the dominant light phenomenon, but only a fluctuating secondary phenomenon. Our photogravure shows this clearly (the original negative appears even more clearly than the photogravure). One sees how the calcium line  $\lambda = 3179$  and  $3159$ , which is not reversed, completely coincides with the reversed coincidence in the case of weak exposure and delicate development; furthermore, how on the same plate after prolonged exposure the line appears shifted to Roth as a result of one-sided broadening, if the development is carried out in this way leads that the broadened line becomes evenly dense.

It can also be seen that exactly the same widening phenomenon occurs in the reverse line. We can therefore say on the basis of our observations that the broadening towards Roth is not only due to the

non-inverted line, but that it also shows the vicinity of the correspondingly inverted line. In the latter, too, the dominant wavelength (characterized by the inversion phenomenon) of the most intense part of the broadened line lies next to exactly the same broadening phenomenon towards Roth, so that "spark reversed" and "spark not reversed" behave quite analogously. Since the reversal phenomenon weakens the most intense part of the broadened line, i.e. gives it light in the negative, the neighboring unilateral widening phenomenon appears all the more powerful, indeed it can happen that the intensely dominating edge of a unilaterally widened line is weakened by the beginning reversal phenomena, that one believes to recognize the neighboring widening phenomenon as the maximum of the line. This is shown by the line  $A = 3181$  on our table; most of the time it is not reversed, and on the basis of the present photograph everyone would in this case (in the case of plentifully exposed plates, such as the middle part of the figure) move the maximum of the line much further towards Roth, if not the (here rather difficult to obtain) Reversal phenomenon would attract attention; this is eccentric to violet.

However, if you examine a strong bottle spark generated with little calcium between carbon electrodes or other electrodes, exposure is very brief, so that you. keeps the actual spectrum as far as possible free of the accompanying side effects of broadening, so we always observed complete coincidence.

On the basis of our experiments, therefore, we cannot regard opposing changes in the wavelengths of the lines in the "spark: 'reversed" and "not reversed" as actually existing; at least they do not apply to the calcium lines  $A = 3159$  requested by Messrs. Exner and Haschek , 3179, 3181, 3706 and 3737. Those of the above on the basis of the apparent displacement of the frozen calcium lines and based on the work of Jewell's, Humphrey and Mohler's

The assumption made that the pressure in the interior of the spark path is enormously increased, appears to us to be doubtful.

Exner and Haschek observed no shift in the lines at  $J = 4302, 4299, 4289, 4283, 4226, 3968, 3933$ . But it is precisely these lines which, according to Humphrey and Mohler's fundamental investigations<sup>2)</sup>, are subject to shifts with increasing pressure. If, therefore, in the calcium spectrum, on the basis of the Humphrey and Mohler studies, an enormously increased vapor pressure is to be concluded, then the ones requested should primarily be requested

1) Heavily exposed lines, broadened somewhat towards violet, give strongly different numbers in the opposite sense.

2) «Astrophysikal Journal», Vol. III, pag. 128.

J. M. Eder and E. V a l e n t a.

Humphrey and Mohler's standards show shifts if one wants to apply the Humphrey and Mohler's conclusions. However, the standards mentioned show according to Exner and Haschek's own findings, as well as our measurements (made with greater dispersion) no shift phenomena. Therefore we consider the assumption of enormous pressure phenomena in the spark path of the calcium spark as not proven and doubtful.

In conclusion we also note that we have repeatedly found experimentally confirmed the observation made by Jewell, Humphrey, and Mohr, that the broadening or shifting takes place with increasing pressure towards Roth. But we believe that there is no reason to assume an enormously high pressure in the spark path if there is no other sentence than the described broadening phenomena in the spark

spectrum of calcium in the air at ordinary pressures. For in some calcium lines we found phenomena which speak the opposite, in that other lines appear broadened according to Roth in the arc spectrum, but remain sharp in the spark spectrum.

Spark spectrum of lithium.

The spectrum of lithium is characterized by its simple construction and the small number of lines both in the arc and in the spark and is (if one considers the entire visible and ultraviolet spectrum) even fewer lines than the sodium spectrum.

The arc spectrum was thoroughly examined by Kayser and Runge 1), they found 18 lines. Exner and Haschek investigated the ultraviolet spark spectrum of lithium using lithium sulfate melted on iron. They could only find three lithium lines ( $\lambda = 2815 \cdot 55$ ,  $3232 \cdot 91$ ,  $4603 \cdot 10$ ) in the whole of the ultraviolet districts 2).

We were particularly interested in the lithium line which Exner and Haschek determined with the wavelength  $3232 \cdot 91$ , because it is cited by those named as one of the proofs (next calcium lines, see above) that line shifts between the arc and spark spectrum are noticeable to whom they found the information in our previous treatise "On the Spectrum of Calcium, etc." quoted

To draw conclusions. We tried to obtain the complete spark spectrum of the lithium  
universe and benzten metallic lithium electrodes (in the air) and a strong fame k o  
rff'schen

Bottle spark.

The metallic lithium was provided to us by Hofrath Professor Dr. Ludwig in the most friendly manner; the same had been shown by himself in an electrolytic way and only traces of magnesium and copper could be detected by spectral analysis in this lithium. The latter did us good in determining the wavelengths, in that the main line of copper, used by Rowland as the standard, emerged as a very fine, sharp line in our spectrum photos and a very precise measurement of the line in question  $\lambda = 3232$  allowed; of course we also took pictures of iron standards at the control.

The recordings were made with our large concave grille. The accuracy of the mostly fuzzy lithium lines should be  $0 \cdot 05$  Angstr 'units, whereas the line  $\lambda = 3232$  measured by us on various briefly exposed lithium plates has probably been increased to  $0 \cdot 02$  Angstr' units. The latter lithium line is namely widened on one side (according to Roth) and blurred in the same direction. Sometimes we got the line reversed, sometimes not. If you measure the center of the non-inverted line, which had been exposed somewhat abundantly, on strongly ("hard") developed plates, you can no longer see the dominantly bright line core from the one

1) Prussian Akad. D. Wissensch., Berlin 1890; See also W a t t's: • Index of Spectra », 1893.

2) Meeting reports d. emperor. Akad. D. Wissensch., Vienna, Vol. CVI, Abth. II, December 1897.

separate weaker broadening on the side and one then obtains strongly fluctuating values averaging  $\lambda = 3232 \cdot 96$ . Exner and Haschek gave this line the value  $\lambda = 3232 \cdot 91$ . If one exposes, however, the line is narrow and can be measured very sharply, and the now constant value of the wavelength was

determined by us as  $A = 3232 \cdot 798$ . If this number is compared to the Kayser and Runge values of the corresponding arc lines with  $A = 3232 \cdot 77$ , the result is a far smaller deviation between spark and arc than Exner and Hasche k found, so that, according to our test results and measurements, the Reason to be able to assume any considerable displacement of this line in the spark spectrum with respect to the arc spectrum. For the line  $A = 4602 \cdot 46$  we found this  $\lambda$  as the mean of 10 determinations with the possible error of  $0 \cdot 05$  Angstr's units; but this line has a peculiar appearance, because the reversal phenomenon (1) is unusually broad, and is therefore difficult to measure, and because, according to Roth, the adjacent part appears too widened. It is thus the phenomenon analogous to the behavior of one-sided broadened lines described in the previous article. Incidentally, come both in archery and funkenspectrum presents lines which have been broadened several times according to Roth, so that this phenomenon does not present any fundamental difference between the two types of spectra.

We could not obtain the lithium line  $A = 2815 \cdot 55$  frozen by Exner and Hasche k in spite of all our efforts when using our pure lithium metal electrodes, although we very clearly photographed other secondary lines, which the above-mentioned could not obtain in their experimental set-up due to low light intensity. In our opinion, the line  $A = 2815 \cdot 55$  must therefore be deleted from the series of lithium lines.

Lithium.

The intensity of the brightest line  $i = 10$ , that of the weakest

= 1..Eder and Valenta

Kayser and Runge

Flame

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Spark pedal

Arc

spectrum

spectru

m1

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I-i

remark i

remark

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1

6708 6103 6708 · 2 6103 · 77 4972 · 11 10 10 4 I seen by us, but not measured 6708 · 2 6703 · 77 4972 ·

11 10 10 5 mostly the other way around "blurred against Roth

4602 4602 · 46 10 reversed, widened according to Roth 4602 · 37 10 reversed

4273 · 52 4 out of focus against Roth 4273 · 44 4 out of focus according to Roth

4132 · 57 6 {out of focus, greatly broadened on both sides 4132 · 4-t 8 out of focus on both sides 3985 90 1 out of focus according to Roth 3985 · 94 2 out of focus according to

Roth

3915 · 2 5 ' ) out of focus, reversed to both

sides 3838 3 1 blurred according to Roth

3794 · 9 4 out of focus on both

sides 3718 9 1 "

3670 6 1 "

3232 · 8 3232 · 798 8 {with short exposure sharp, with longer exposure widened according to Roth 3232

· 77 8 mostly the other way

round 2741 · 57 2 2741 · 39 5 "

2562 · 60 4 "

2475 13 4 "

2425'55 2 "

2394 54 1 "

1

1) The light stripe in the spectrum negative. J. M. Eder and E. Va 1 e n t a, Spark spectrum of calcium and lithium.

A comparison of these three spectra reveals that the flame spectrum naturally has very few lines, whereas the spark and arc spectrum differ less among themselves than is the case with potassium and sodium. We did not find a single lithium line in the spark which would differ with characteristic brightness from the arc spectrum, while in the sodium and even more so in the potassium spark spectrum many characteristic lines appear which are absent in the arc. The increase in bright lines in the spark spectrum as opposed to the arc spectrum seems to have a certain connection with the atomic



weight of this group of elements, since this phenomenon occurs most strongly with potassium, less with sodium, and even less or not with lithium.

Spectral analysis of the luminous gas  
flame. Of

J. M. Eder and E. Valenta.

(Presented at the meeting of the Imperial Academy of Sciences on July 7, 1898.)

Since the year 1856, several investigations have been made about the spectrum of the hydrocarbons burning in air or oxygen with a weakly luminous flame, namely the blue flame cone in the flame of the Bunsen gas burner, which have been carried out on the visible as well as on the ultraviolet part extend. The latter was discovered by one of us in 1886 using a glass spectrograph, and in 1890, at the same time as the visible spectrum was examined by means of a quartz spectrograph of low dispersion (a quartz prism), the spectrum photograph was published and the wavelengths of the most important characteristic lines and bands were measured 1). In the meantime the treatise by WN Hartley has appeared, "Flame Spectra at highest temperatures", Part. I (Philos. Transact. Royal Soc. London, Vol. CLXXXV [1894], p. 161), in which the spectrum of the oxygen luminous gas flame is described; Hartley did not take into account the work mentioned at the beginning or did not know it.

However, the positions of the "marking-like sharp lines" given by Hartley differ significantly from the earlier information.

The most characteristic blue carbon band in the SW spectrum, which begins particularly conspicuously at  $\lambda = 4737$  (and was found by us to be identical to the "fourth carbon band" Kayser and Runge's in the electric coal arc), is not mentioned by Hartley, unless one assumes that there are measurement errors of incidentally of whole angstrom units, that is, they are Hartley's numbers)  $\lambda = 4732$  and  $4720$  imprecise values of the prominent edges measured by us)  $\lambda = 4737$  and  $4715$ . On the other hand, however, speaks the fact that Hartley himself considers these lines to be different from the Kayser and Runge edges and does not cite the latter as comparable.

Hartley differs from all previous spectral analysts on numerous similar main points (Swan, Angström, Thalen, Hasselberg, Lecoq, Eder, etc.)

But since we always found these bands (edges and groups of lines) very clearly and with the most varied of apparatus (quartz and glass spectrograph, small and large concave grating), we had to assume that Hartley's wavelength measurements were very imprecise. The same one worked

namely with a very wide slit and a quartz prism, which both circumstances, when they work together, preclude an exact definition.

This is the only way to explain the fact that Hartley lacks the characteristic group of lines (apparently single lines)  $\lambda = 4324$ , which one of us also found with a quartz apparatus at the time and was ascertained in our subsequent work with the grating spectrograph; Likewise, the ultraviolet band is found in Hartley so mutilated that the matter needs to be clarified. We therefore subjected the oxygen luminous gas flame not only to a renewed examination with the quartz apparatus with a very narrow gap, but also with our bright grating spectrograph with a short focus, and finally with the large grating with a long focus (radius of curvature = 15 feet English) a renewed careful examination Investigation in order to obtain exact values for the wavelengths of the luminous gas flame (blue flame cone).

We let oxygen enter the luminous gas under a pressure of  $1/4$  to  $1/4$  atmospheres by means of a Linnemanian blower, so that a bright blue flame cone emerged, which emits the spectrum in question most clearly, while the upper, colorless part gives only the oxyhydrogen spectrum. In other series of experiments we reduced the oxygen supply to a minimum, so that a blue cone was just created, and finally we also worked with the usual luminous gas Bunsen burner in order to study the character of the Spectra at a relatively low temperature. In the latter case, the exposure time varied from 6 to 12 hours to eight days; the comparison spectrum (iron sparks) was photographed at the beginning and at the end of the experiments and only those plates were used for measurements in which the inaccuracies of the results due to temperature fluctuations during the experiment did not amount to more than about 0.05 angstroms. With a very abundant supply of oxygen and the relatively high temperatures caused by it, not only do the edges of the bands emerge more clearly, but numerous fine lines appear next to them (when using the grid spectrograph with large dispersion); the continuous spectrum, with which the edges of the bands are apparently shaded in the case of smaller dispersion, consists of groups of lines, which become clearer the closer the combustion temperature is. At relatively low temperatures, especially with the Bunsen flame (luminous gas and air), the shaded groups of lines are strongly blurred, so that they appear almost as homogeneous shading and the lines that converge at the edges then form dark stripes, which are already earlier photographed and reproduced 1).

Despite these fluctuations, we were able to identify the underlying type of spectrum of the luminous gasflame under all circumstances.

The accuracy achieved by us using our large concave grating (spectrum of the second order) differs according to the sharpness of the line groups. The sharper lines of the characteristic violet and ultraviolet main bands  $\lambda = 4314$  to  $3871$  should not be afflicted with measurement errors greater than  $0.01$  to  $0.02$  Angstr's units, while the less easily photographable lines in the violet band - measurement errors of incidentally  $0.03$  Angstrm 'see units should contain, whereas the blue-green bands ~ appeared a little less precisely on our photograms (we used iodine-bromide silver plates, since pure bromide-silver plates in this area, around  $\lambda = 4700$ , are already less sensitive), perhaps in the worst case errors to  $0.07$  have Angstr units. The finer and more indistinct lines of the shaded bands partially eluded the measurement of the latter band, so that the number of them is actually greater than the lines still plentiful in our table; rigens, they are completely sufficient to characterize the spectral band.

1) Ver ~ !. pag. 1 of these dependencies.

Our new measurements, which probably determine the spectrum of the oxygen luminous gas flame (Swan's spectrum) with far greater accuracy than all previous measurements, leave no doubt as to the arrangement of the bands. From this it follows that the characterization of the Swan spectrum given in Ed's previously cited paper (in the visible and also in the ultraviolet part) was completely correct and agrees far better with the results of our results with the large grating spectrograph than Hartley's information.

The relationships of the spectrum of the oxygen luminous gas flame assumed by Hartley on the basis of his inaccurate measurements are no longer valid if they are exactly the numbers of our much better defined spectrum uses.

Hartley believed to find the Kayser and Runge'schen cyan bands  $A = 4215, 4208$  etc. of the electric carbon arc light in the oxygen luminous gas flame. On the other hand, our measurements show without a doubt that the violet cyan band beginning with  $A = 4216$  with the violet luminous gas

Fig. 36.

Gang ~ gang \

"~ C"

... " ... C ~ ...

Part of the spectrum of burning hydrocarbons.

Flame spectral band (') has nothing in common 1) and only imprecise measurements can lead to such erroneous conclusions. The spectrum analysis of the spectrum of the oxygen luminous gas flame (Swan's spectrum) gave us the following results:

The yellow ( $\beta$ ), the grey ( $\gamma$ ) and the dreadful blue (band of the Swan spectrum of burning hydrocarbons consists of several edges shaded to violet, which turn out to be composed of numerous fine lines with good resolution. The same, as well as the band ( $\epsilon$ ) they are also found with surprising agreement in the spectrum of the electric carbon arc, and probably also in the burning cyan gas. It is therefore very likely that there are fairly general components of the carbon spectrum occurring under different conditions, or certain forms of it.

The grey band  $\gamma$ , as well as the blue one, contain, in addition to the characteristic edges, many fine lines, which continue towards the violet side of the spectrum and clearly appear with very long exposure and intensive combustion of the luminous gas.

In the violet, the edges of the carbon bands of the electric carbon arc appear only fragmentarily (4380, 4372, 4365) and disappear when the flame is lively fanned with oxygen.

1) Which has already been confirmed in the previously cited treatise, pag. 1. 44 \*

J. M. Eder and E. Valenta.

On the other hand, the specifically characteristic ultraviolet bands (up to fl) of burning hydrocarbons begin there, which typically distinguish this type of spectrum from the electric carbon arc. This main band in the spectrum of burning hydrocarbons first discovered by us is missing in the electric carbon arc, but appears to be found in the burning cyan gas.

We show these important bands as an exact facsimile of the photograph obtained with the large grating spectrograph in Fig. 36 on page 347, while the exact wavelength of the lines in question is given in our table.

In addition, we also note that the ultraviolet water bands, which always occur intensively in the luminous gas flame, can always be very clearly detected; when working in the second-order spectrum in the blue-violet, they have to be filtered off through strong, greyish glass.

In the table below we give the wavelengths of the Swan spectrum that we have determined (excluding the water bands). Since in the usual laboratory work with small prism spectroscopes one can usually only observe the poorly drawn up carbon bands and the completely drawn up spectra give a strongly deviating overall impression, it is useful to determine the position of the edges (apparently rather sharp individual lines or lines combined into groups) ascertain. That is why we have included a rubric for the apparent appearance of the Swan spectrum with a small dispersion.

We have dispensed with comparing Hartley's numbers in our table, because the former are so highly imprecise that a comparison seems impractical.

Wavelength measurements in the spectrum of burning hydrocarbons. (Swan's spectrum.)

Rowland's Units. -- The intensity (i) of the strongest lines = 10, that of the weakest = 1). The spectrum of chlorine 1). Of

J. M. Eder and E. Valenta.

(Presented at the meeting of the Imperial Academy of Sciences on April 13, 1899.)

The spectrum of chlorine appears under various conditions in variable forms, most completely when the electrical spark breaks through by Plücker's sounds at reduced gas pressure, further when the bottle spark is broken through by chlorine at atmospheric pressure, and when the electric spark acts on aqueous hydrochloric acid or chlorides (with a short discharge spark). All these phenomena were observed several times and described qualitatively. The available wave measurements of these spectral phenomena are, however, very imprecise and cover a small area of the spectrum, as do some of the drawings published so far

Fig. 37.

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"" Chlorine spectrum according to W i l l i g e n's  
drawing.IB

of the spectral phenomena is so uncertainly oriented that it is hardly possible to compare the individual data available with one another, even approximately.

Under these circumstances and in view of the fact that :: s the ultraviolette chlorine spectrum is completely unknown, we subjected it to a precise examination by means of our large grating spectrograph.

Since the earlier works that exist relate to our measurements, we will briefly mention them: In his observations on "On the Electric Discharge", P i e k e r states that the spectra of iodine, bromine and chlorine show a strange analogy 2); however, he knew the spectrum of chlorine

1) A provisional report; about a survey of the chlorine spectrum that we carried out, presented at the meeting on November 17, 1898, can be found in Akademie-Anzeiger No. XXIV. The lengths given there are replaced by more precise values in the present paper.

2) Poggendorff's • Annals for Physics and Chemistry », 1858, Bd. CV,  
p. 83. but did not draw exactly at the time.

Van der Willigen<sup>1)</sup> had better results. In 1858 he made remarkable observations. Pay attention to the spectrum of the chlorine gas at atmospheric pressure or less Dilution on. He worked with a Ruhmkorff and Condensator and formed the

lines observed by him (see Fig. 37 on p. 358). 425

The yellow sodium line ("Sodium") is shown as a guideline. Left

of this is the red part, to the right the large and the green-blue; blue

and Violet could not observe Willigen because his spectra were too low in  
brightness: \_ 433434

respect, think highly of. Willigen's drawing is not very precise; at least one recognizes by the same tl:

the general appearance of the spectrum of chlorine in spectroscopes of very small dispersion pretty good. We put the same under the lines in question the wavelengths which we consider to be appropriate, in so far as Willigen's sketch Orientation facilitated.

Plücker later came back to the Spectrum in association with Hittorf of the chlorine 2). You received a powerful one when the spark struck you Ruhmkorff's inductorium always only a line, never a band spec 452

strand, preferably with about 60 mm pressure in the Geissler pipe; they state that 457 the spectrum of chlorine gradually fades at lower pressure (similar to bromine). In

In a careful drawing (Fig. 38), Plücker and Hittorf give the picture of Chlorine 474 spectrums, as they can be achieved by means of a prism spectroscope of comparatively large 479

{481

Saw dispersion. 482

The not very precise wavelengths of these lines are taken from Watts «Index \$" .. c: ~~~~~; 489 of Spectra », 1889, p. 18 and include them in our tables for comparison. To .. U 1 =

those lines of Plücker-Hittorf's drawing, which we believed to be certainly identical 1 i

To be able to fix, we set our \ Wavelengths of the chlorine, so that the Drawing now appears general-oriented.

G. Salet<sup>3)</sup> found that the chlorine spectrum · when the electric

Easily and with great sharpness obtained by means of chlorine gas at atmospheric pressure {521 522 can be. If one uses the Ruhmkorffian inductorium, they become

Spectral lines a little blurry and. some metal lines appear in the vicinity 539 of the electrodes. (542 <544

According to Salet's statement, these themselves heat up much less when used 1545 a Holtzian influence machine and only the chlorine lines appear.

The work

With vacuum pumps and mercury air pumps, Salet found it very difficult and stayed 571

therefore when using the Holtz influence machine 4) and atmospheric pressure.

578 Except for small ends, he melted the platinum electrodes of the chlorine rod into a glass rod

.. ~ = =

and attached them a few millimeters to each other. During the overturning 1 =====  
1 593 of the spark, he ran chlorine gas through the glass tube and then melted the  
pipe shut. 609 Under these circumstances the spark gave a bright bluish-white light.

1) Poggendorff's "Annalen f Physik und Chemie", 1859, vol. CVI, pag. 610.

2) «Philosopher. Transact. of the Royal Soc.>, London, Vol. CLV (1865), p. 24.

8) Salet: «Anual de Chim. et de Phys. •, Paris 1873 (IV.), vol. XXVIII, pag. 24.

4) About the influence of the induction machine when switching on smaller or larger spark  
gaps ~ 665 on the spectral phenomena in comparison with the spark spectrum Glory of  
Korff's Inductories 675 makes Hasselberg: «The second spectrum of hydrogen», Mem. de  
l'acad. de sciences de St. Peters bourg, ser. III, vol. XXXIII, no.7, 1882, remarks.

J. M. Eder and E. Valenta.

In his treatise ("Les spectres des metalloides", Paris 1872), Saidet reproduced the obtained  
chlorine spectrum, which drawing, however, does not completely coincide with a later drawing  
of the chlorine spectrum by the same author. In his work "Traite elementaire de  
Spectroscopie", Paris 1888, pages 188 and 216, the author mentioned apparently made some  
corrections and accepted the drawing reproduced in Fig. 39 as a representation of the visible  
spectrum of chlorine. In it are parts of the scale below

Fig. 39.

Spark spectrum of chlorine according to Salet's drawing.

his spectral apparatus, wavelengths entered above, and thus orientation is possible. Salet's  
data relate to a not particularly well defined spectrum of the chlorine (prism apparatus) and the  
determinations of the wavelengths are imprecise.

Some wavelength measurements in the chlorine spectrum were carried out by Angström (1),  
furthermore by Hasselberg, who demonstrated the chlorine spectrum in connection with  
Angström's table of chlorine lines as contamination of the glass spectra when vacuum tubes were  
used from chlorine-containing glass (2). We included the statements of both spectroscopists in  
our table for comparison.

In his work "Specters lumineux", 1874, Lecoq de Boisbaudran gives a drawing of the spectrum  
that occurs when the induction spark of short length is flashed between platinum wires and  
aqueous hydrochloric acid. It gives the wavelengths of some chlorine lines with  $\lambda = 5457$ ,  
5445, 5421, 5390, 5216, 5103, 5079, 4919, 4897, 4817, 4797, 4787, 4775. In addition, platinum  
and hydrogen lines appear.



Eugen Demarcay 3) photographed the same spectrum of aqueous hydrochloric acid between platinum electrodes (Ruhmkorff sparks) at atmospheric pressure and short sparks by means of a glass prism spectrograph and identified in the same only the chlorine lines) = 4819.7, 4810.6 and 4794.7. On the basis of our analysis of the spectrum of chlorine, however, more lines of chlorine can be identified in sparks of aqueous hydrochloric acid.

Very meritorious investigations into the behavior of the chlorine spectrum at different pressures from Ciamicion, which unfortunately describes his observations only in the form of a drawing that is related to an arbitrary scale, which is not exactly drawn out. Since the reduction of his information to wavelengths of the chlorine lines is not easy under these circumstances, we began to write in his spectrum drawings the lack of orientation numbers of the respective wavelengths of particularly characteristic groups, and we succeeded in making these tables useful for discussion. Even if Ciamician's drawings are only qualitative for spectral analysis, they are valuable in this respect because they actually show the changes in the chlorine spectrum with increasing pressure and the comparatively small dispersion of the

1) «Camp. rend. », vol. LXXIII, pag. 369; See also Watts: "Index of Spectra", 1889, p. 37.

2) Hasse 1 b e r g observed the appearance of lines of chlorine in a strongly evacuated goose after a prolonged penetration of the spark, which element probably got from the (chloride-containing) glass into the vacuum tube (Bull. de l'acad. de St. Petersburg, 1881, p. 405).

3) Demarcay: • Specters lumineux », 1895, Paris.

Bring the prism apparatus to view quite well. That is why we also reproduce the Ciamician drawings 1) with our subsequent entries of the wavelengths.

According to Ciamician ("Sitzungsber. D. Kais. Akad. D. Wissensch.", Vienna 1878, Vol. LXXVII, Abth. II pag. 839) the spectrum of the three halogens offers analogous peculiarities in her printing; the lines appear faded, sometimes a little thicker, without it being possible to speak of an actual band-like widening of them. In addition, there is a continuously illuminated background, which increases in brightness with the printing and often the lines themselves shine. This latter relationship is most evident in iodine, where the continuous spectrum ultimately reveals everything else. In the case of chlorine and bromine, individual lines still shine out of the continuous spectrum. The behavior of certain lines in the red field with chlorine and bromine, which always retain their full sharpness and delicacy, is remarkable.

Of interest are the Ciamician's data on the changes of the relative intensity of the spectral lines to each other with different pressures. "If you want to compare the halogens with each other," says Ciamician, "in order to determine the homology and only use the spectra of the dilute vapor in Geissler's tubes, then that is connected with considerable difficulties, since one the lines can only be compared in groups, and these lines often have so different intensities in each of the three elements that one can be in doubt whether the homology is really to be understood in this sense. These differences are due only to the variability of the intensity and number of lines with the pressure. It can always be changed by changing the pressure of the gas or vapor to obtain spectra, which show the perfect homology of the lines. So one must apply that tension to iodine; which equates to a saturated iodine vapor atmosphere of 50 to 80 ° C., but with chlorine and bromine atmospheric tension.

In a later treatise he made the influence of density and temperature on the spectra of gases and vapors, Ciamician ("Sitzungsber. D. Kais.Akad. D. Wissensch.", 1878, Vol. LXXVIII, Abth. II [July]) the fluctuations in the spectrum of chlorine attentively. He describes them in the following way: In strongly evacuated chlorine he received a spectrum (Plate XVIII, Fig. 2, No. 1), where A and B are groups of red lines, ii a group of weak lines in green, g, h, i, k and the double line l are the largest main lines, while -E represents seven strong blue lines. Group B changes at 500 to 600 mm (see Plate XVIII, Fig. 2, No. 2), and a continuous spectrum appears there, while in the green some lines (especially the double line 1) become blurred. The spectrum of chlorine at atmospheric pressure reveals No. 3; A continuous, illuminated background appears and two new, strongly blurred stripes (a, b, Plate XVIII, Fig. 2) appear together with other bands in the Gr (in place of the earlier group Li). With a further increase in pressure from 150 to 180 cm there are no significant changes, only a few stripes become clearer and there is an insignificant line increase (Plate XVIII, Fig. 2, Nos. 4 and 5). The continuous spectrum becomes extremely bright, so that lines a and b are almost illuminated. The line c becomes very blurred, less so the four lines of group C ". The lines of groups A 'and B' remain perfectly sharp, almost as well as D" and E. Switching on Leydener bottles did the same thing in Ci am ici an's experiments, as did magnification the density of the gas.

Aubel's attempts to influence the influence of magnetism on the spectrum of chlorine should also be mentioned. Van Aub e 1 brought the capillary of a bottle filled with chlorine gas between the cylindrical poles of a strong, upright electromagnet through which a current of 25 to 30 amperes flowed. The spectrum of chlorine (spark of a

1) These drawings are available in lithographic reproductions. The different chlorine spectra (1 to 5) are originally distributed on two tables, and the scale of 1 and 2 does not entirely agree with that of 3 to 5. However, since the analogous groups from Ci am i c i an were designated with letters, orientation is still possible.

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Ruhmkorff with a Leydener bottle) changed the appearance; new light lines appeared, others became weaker 1). These phenomena are attributable to the change in electrical resistance caused by the magnet.

Morren observed the absorption spectrum of chlorine when using 2 m long tubes 2). He used an apparatus with ff flint glass prisms and found numerous lines from red to blue.

None of these reactions have hitherto been used for practical spectral analysis, but indirect methods of detection have been suggested for the detection of chlorine. On spectral analysis of chlorine and bromine by means of flame reaction of barium chloride, see Le c o q de Boisbaudran: "Compt. rend. », 1880, vol. XCI, pag. 902 4).

In order to obtain a precise knowledge of the line spectrum of chlorine, we worked with the help of a large R o w 1 on the concave lattice and extracted chlorine lines with various dimensions (10 to 100 mm). We observed that the brightness of the capillary in the P 1 c k er 'see, pipes filled with chlorine is

greatest at about 50 to 100 mm pressure, but the lines are already subject to very strong widening phenomena.

At about 30 mm of pressure (mercury column) the brightness of the spectral phenomenon is still noticeable; the glowing light is dreadful, the color of the capillaries more blue, whitish when the current is strong, the lines are moderately broadened, and the sharpness of most of the lines is wrong. At 10 to 20 mm pressure the brightness of the chlorine is noticeably lower, but it is still sufficient to obtain well-defined spectra with perfect sharpness of the lines with exposure times of 3 to 10 hours in the grating spectrograph with the tubes set up longitudinally. At 5 mm, on the other hand, the light is already so weak that we could no longer expose it to the end. At pressures greater than 100 mm, the resistance of the chlorine gas is so great that the spark can only break through with difficulty and the electrodes have to be brought closer together.

Small impurities in the chlorine with nitrogen are a problem at lower gas pressures. The band spectrum of nitrogen occurs. With decreasing gas pressure, nitrogen seems to take more and more the conduction of electricity and the nitrogen spectrum begins to dominate (at 10 mm pressure and below), while at this pressure (and constant mixing ratios) the chlorine spectrum strongly dominates and the nitrogen spectrum is hardly noticeable. Such observations should be useful for the applied spectrum analysis.

Working with chlorine on the spectrograph is time-consuming and slow, as it is only possible in a few cases to obtain a photo that is sufficiently exposed.

Platinum wires have proven themselves best as electrodes, because they are only slightly attacked by completely anhydrous chlorine, as long as the electrodes do not come into the glow. But as soon as stronger stress makes the wires smooth, the absorption of chlorine becomes so strong that the rings turn into a haze.

1) D'Alembert: Journal de Physique •, 1898 (III), Vol. VII, pag. 308. The spectrum of bands of a mistress was also changed in the magnetic field and converted into a shiny spectrum of lines, and next to the cathode there was a great fluorescence. These phenomena disappeared with the rise of magnetism. The spectrum of chlorosilicon also changed under the influence of magnetism.

2) • Compt. rend. de l'acad. de sciences •, Vol. LVIII (1869), pag. 376.

3) H. Vogel: "Practical Spectral Analysis of Earthly Substances", 2nd ed., 1889, Vol. I, p. 321.

4) When freezing chlorammonium or introducing hydrochloric acid gas into the flame under a barium oxide sample already in it, characteristic lines are obtained. Leconte found that these lines also appear in a barium carbonate spark spectrum if the lung of a chlorine-containing substance is dripped onto the barium carbonate, the liquid is made to evaporate, heated to a red glow and then the spark is killed. In this way, 1/9000 milligrams of chlorine should still be detectable. Vogel: "Practical Special Analysis of Earthly Substances", Vol. I, 1889, p. 156 and 188.

Time becomes unusable, with the resulting chlorine platinum sputtered (dusted) and the glass wall makes opaque. But if the current is weak in the case of strongly evacuated chlorine gases, then here is brightness very low and you therefore have to work at the limit of the permissible current strength, where half one is exposed to many stunts.

If the Leydener bottles are switched on, the chlorine gases perish more quickly; we had to hence begin with the analysis of the chlorine spectra by means of inductorium without Leydener bottles. Runners with dry chlorine or hydrogen shone best at 5 mm pressure, at 20 to 30 mm bad. The hydrogen chloride dissociates so quickly that the spectrum of chlorine is only very brief

Time can be observed, since the same will soon be drowned out by the spectrum of the released hydrogen.

We determined the wavelengths of the chlorine lines on the second order spectrum, related them to Rowland's standards<sup>1)</sup> and compiled the results of our measurements in the following tables (p. 364 to 368).

If one compares the appearance of the chlorine lines in the spectra with different prints, which is possible with the help of the tables and our heliographic figures<sup>2)</sup>, then there are variously spreading phenomena and variations in the brightness of the lines. In this print the continuous spectrum appears, of which Ciamician already spoke.

We were no more able than our predecessors to observe the occurrence of a band spectrum in the event of a spark discharge caused by Plicker's sounds. It is noteworthy that, although many lines in the chlorine spectrum are variable, on the other hand there are also numerous lines which are very stable.

The four chlorine lines (main lines in yellow size)  $\lambda = 5457, 5444, 5423, 5392$  are apparently fairly constant in the line spectrum of chlorine. They are found both in highly diluted chlorine and at atmospheric pressure, as well as in the spark between hydrochloric acid.

When observed by means of a spectroscope of low dispersion (1 to 2 prisms) these lines appear almost unchanged in sharpness; In our original experiments with the large grating and second order spectrum, however, we recognized that these lines can be broken down into sharp, fine triplets and doublets at low gas pressures (in the chlorine tube of about 10 mm pressure) (see our tables, also plate XX, Fig. 1). At about 20 to 30 mm of pressure, these triplets become blurred, as their weakest line, which is difficult to identify, widens and merges with the closely adjacent line 3). A blurred doublet remains (see Plate XIX, Fig. 2), which appears as a simple, somewhat blurred line with increasing pressure. This is not very much subject to further spreading phenomena, so that the yellow-green lines of the chlorine can be regarded as characteristic.

The same applies to the large double lines),  $\lambda = 5221$  and  $5218$ , to the lines).  $\lambda = 5103$  and  $5078$ . The blue groups).  $\lambda = 4819, 4810, 4794$ , which group is easy to photograph.

The line appears in purple),  $\lambda = 4132$  als main line, which was noticed by all previous spectroscopists only by Salet; at the beginning of the ultraviolet, however, the group around  $3860$  is particularly characteristic, but the latter is subject to enormous widening with increasing pressure. It is only possible to keep these lines sharp and some of the

1) We chose the Rowland iron lines of the solar spectrum (Rowland: "A preliminary table of solar spectrum wave-lengths", Chicago 1898) because they represent a completely closed system of lines comparable to one another, the reduction of which to any other standards is very easy is possible

2) Spectrum photographs of the chlorine have not yet been published at all from other sources.  
") From the triplet at 5457 first blurs with increasing pressure), = 5457 \* 6 and unites with), = 5457 \* 7 to

a line shaded according to Roth, then 5456 becomes blurred, and with strong pressure they flow together to form a line. 46 \*

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the same in clear double lines. Plate XX, Fig. 3 shows the practical breakdown of the double line A = 3851 x 1 and 3851 x 2, furthermore 3845 x 8 and 3845 x 5 (photographic enlargement of the spectrum photograph). With a slight increase in pressure (approximately 20 mm) these lines widen towards red and blur into one another (Plate XX, Fig. 4, upper part); with stronger pressure, about 30 mm, the broadening increases (Plate XIX, Fig. 3 ) and at about 50 to 100 mm they widen like a ribbon, shift noticeably towards Roth and a continuous spectrum appears (Plate XX, Fig. 4, lower part.)

Most, but by no means all, of the lines of the line emission spectrum of chlorine are subject to these broadening phenomena. In the chlorine spectrum there are individual lines which elude the one-sided broadening phenomena according to Roth and almost retain their sharpness even with increasing pressure or broaden evenly on both sides and thus maintain their wavelength constant, for example the secondary line A = 3750 (Plate XX, Fig. 4); Since most of the chlorine lines react noticeably to different pressures, even a small pressure difference changes the character of many areas of the chlorine spectrum, as already stated by Ci on the ici and as we can see on Plate XIX, Fig. 2 and Plate XX, Fig. 1 represent more clearly. The former spectrum was obtained with a chlorine tube which was under a pressure of about 30 mm, the latter at about 10 mm.

The spectral photographs at low pressures not only show greater sharpness in general, but also show variations in intensity and perhaps some new lines. In view of the great difficulties in determining the respective pressure in the chlorine spectrum, we began with the indication of the illustration of the phenomenon through photographic images and the recording of the measurement results of the spectral regions of the chlorine spectrum examined by us.

Wavelength measurements in the spectrum of

chlorine. Eder and Valenta

Older observations

Chlorine 10 to 20 mm print i remark chlorine 30 to 40 mm print chlorine 70 to 100 mm print remark Sale

~ r Hassel: lker l Thalen 1 berg ---

~ -) ,.1 i remark

1 seen by us, but not measured 5672 · 2½ 5635 · 1 1 widened 5625 · 5½ 5623 · 1½ 5580 · 1½ 5570 · 4½ --

-- indistinctly widened 6670 {6110 6758 '8 6711 · 1 6681 · 4 6657 · 1 6093 · 4 Mainline 5937 · 6 5930 · 5

5785 · 4 5714 · 0 5681 · 1 5669 · 0 5635 · 1 5596 · 2 5593 · 5 5572 · 4 5536 · 4 5529 · 3 5527 · 7

5457 · 70 ½ sharply according to Roth ver 5457 · 70 ½ widened l

5457 x 28 3 "5457 x 30 3 one meter wide (strip 5460 5456 x 1 5455 x 5 5456 x 7  
5456 x 391 2 "5456 x 49 2 J

1) Schuster considers the variable chlorine spectra observed from Ci am ici to be several different spectra lying one on top of the other (• Rep. Brit. Assoc. •, 1880, pag, 269; see also K a y s er:  
«Spectralanalysis •, 1883, pag.

256). Older observations

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Valenta'

Chlor Hassei-Chlor Chlor Salet 1 Pllicker 1 Thalen70 to 100 mm berg10 to 20 mm print 30 to 40 mm printprint

In the second case, the breakable lines appear very sharp and one obtains the spectrum corresponding to the high temperatures. In this case it will releases less heat, but it is distributed over a smaller quantity of gas.

The pitch lengths determined by Sa1et, which we have included in our table are not very accurate.

We owe the first detailed experiments on the influence of the density and temperature of the bromine vapor on the spectrum of the same to Ci am i c i an 1). He found that different spectra were obtained according to the degree of dilution. If the temperature is increased sharply, the spectrum is obtained, Plate XXI, Fig. 1. This spectrum shows certain peculiarities with regard to the red part.

At ordinary temperatures and pressures corresponding to them shows the bromine in the red field apart from the group of lines A '(Plate XXI, Fig. 3) two intense lines. (a and b). These lines become weaker and weaker as the thinning proceeds. With a print of 10 mm they are still present, with further dilution they become very weak and, according to Clamician, two new lines (v, and v) appear.

The spectrum of the bromine vapor at the density which it possesses at ordinary temperature differs from that of the strongly diluted vapor also by the complete receding of group D ', while from group D "the line 1n remains (Plate XXI, Fig. 2).

If the density is increased by slowly heating the tube, the following phenomena appear in the large field: the lines d, e and f, which appear very intensely in the spectra of the diluted vapor, become stronger and stronger until they reach 30 ° C. appear just as strong as the lines of group D, and two lines appear (y and d. Also the violet lines of group E (p and q) increase their relative intensity compared to lines n, o and r, while the lines of group A 'appear weakened in the red field (Plate XXI, Fig. 3). When the temperature rises further, a continuous light gradually appears, especially in the red field, while the lines lose their sharp borders and become obscured

) Cia 111 ic ian: «Influence of density and temperature on the spectra of vapors and gases», sessionber,the lqis. Akad. D. Wissensch., Vol. LXXVIII, Abth, U, Jqli 1898.

Plate XXI.

Representation of the spectrum of the bromine at different pressures. After a lithographic drawing by Ciamician's, 1878.

Absorption spectrum of bromine according to Hasse1 b erg.

wash appear. The lines of groups B, C 'and D' '(Plate XXI, Fig. 4) appear most broadened, less those of group C' 'and even less the purple lines of group E, while the red lines of A' A "always retain their full sharpness. On further heating, the lines of groups B, C 'and D" appear comparatively less blurred, with a sharper line emerging in the middle of the washed-out stripe (Plate XXI, Fig. 5). The lines cannot be broadened much by further heating, but the intensity of the continuous spectrum increases, so that at a temperature of 200 ° C. it becomes dazzlingly strong and all lines, with the exception of the red ones, from A 'and A "shines (Ci am ici an).

Ci am i c i an 's drawings are on an arbitrary scale; he did not carry out any wavelength measurements, so that his statements are difficult to compare with the other observations.

The absorption spectrum of the bromine vapor was examined by Dani e l and Mi 11 e r1), R o s c o e and Th o r p e 2), Mo s e r 3), but most extensively by Hasse I b erg4). The latter not only made the most accurate wavelength measurements, but also published an excellent drawing. the absorption spectrum consisting of innumerable fine lines. Since this drawing relates to our own findings, we reproduce it on a greatly reduced scale (light pressure) together with the corresponding scale of the wavelengths (Plate XXII).

Hasse1 b erg observed the absorption spectrum of the bromine vapor at room temperature (the Bromine gas was contained in tubes closed with plane-parallel cover plates by means of a large one Lattice apparatus and photographed the second order spectrum in which the cannellations, the one sees with apparatuses of low dispersion appear completely broken up in lines. As a light source the sunlight served and Hasse1 found the lines of the solar spectrum as standards f his measurements.

Our experiments were carried out with P 1 cker's balls, the balls of which were 6 cm in diameter

and were set up longitudinally. The excitation took place by means of the spark of a large one  
Glory of Korff's inductorium without Leydener bottles. The line spectrum of bromine  
appeared more clearly

brightest and sharpest with a print of 8 to 10 mm. At even lower pressures were  
the lines probably sharper, but the entire phenomenon lost its brightness, so that the  
photographi shots presented great difficulties. With 10 to 15 mm pressure the brightness is  
noticeably higher and the lines are still sharp enough.

1, 2 and 4 of the accompanying heliographic plate XXIII are reproductions of  
Spectrum photographs which we made for this print.

Most bromine lines begin to widen at a pressure of 15 to 20 mm;

analogous to the observations in the chlorine spectrum, a11e lines are not found here to  
the same degree

seized by the broadening, but some lines (sometimes stronger, sometimes  
weaker) resist the lateral widening better with increasing pressure.

In addition to the line spectrum of bromine, we observed, especially at low pressure, for  
example in our Bromrren from 8 to 10mm print, a continuous spectrum, which is especially  
in violet

1) Poggen d: "Anna!. D. Phys. U. Chem. •, Vol. XXVIII. Pag. 386.

2) «Philosopher. Transact. », 1877, vol. CLXVII, pag. 209.

3) Poggend: «Anna !. d. Phys. and Chem. ", Vol. CLXX, pag. 188.

")" Mem. De l'Acad. De St. Petersburg ", 1878, Vol. XXVI, No. 4. Furthermore, the  
detailed second treatise Hasse 1b er's" Investigation of the absorption spectrum of  
bromine "(Kongl. Swenska Vetenskaps Academiens Handlingar, 1891, Vol. XXIV, No. 3).

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and at the beginning of the ultraviolet appears so bright that it causes an intensive blackening of  
the photographic plate (see Fig. 5 of the heliographic table XXIII).

This glow of the bromine vapor with the emission of a continuous spectrum becomes clear at),  
= 4300, increases gradually to  $A = 3700$  and further into the ultraviolet. In the area of) .. =  
3700, this continuous spectrum becomes so enormously bright that only the strongest lines of  
the line spectrum meet it.

There is no absorption phenomenon of the line spectrum through the self-luminous bromine  
fumes and



also the strongly orange-yellow colored bromine vapor, which filled the rather large spherical approaches of our bromine, did not dampen the light phenomenon noticeably. This continuous spectrum of the bromine vapor seems to have a minimum between), = 4200 to 4900 and then to rise again at) ..> 4900; this can be seen from our spectrum photograph, Figs. 4 and 5, Plates XXIII. With a gas pressure below 8 mm, this phenomenon seems to fade, as does a pressure of 40 mm. We could not precisely determine the most favorable conditions for the emergence of these luminous masses, which are characterized by a continuous spectrum; In any case, there is a spectral phenomenon which is completely separate from the line spectrum.

The same case occurs with bromine, of which Hittorff) and especially Kronen 2) speaks with regard to iodine, namely: «The Rre shines without its content noticeably absorbing the emitted light; the glow does not therefore take place under the conditions of Kirchhoff's law ». With a print of about 45 mm, the actual line spectrum of the bromine arises in Bromrren when the spark is struck (without bottles) with a simultaneous noticeable broadening of the lines (see Fig. 3, Plate XXIII). At the same time a new band spectrum appears, which penetrates the spectrum mentioned above with a fairly high level of brightness; Fig. 3, Plate XXIII, shows the heliographic reproduction of this band spectrum that we found. The same represents a third spectrum of bromine and probably corresponds to the normal band spectrum, such as sulfur, nitrogen, mercury, etc. . exhibit, while such a band spectrum could not be found with chlorine so far. The emission band spectrum of bromine, which the older spectral analysts had not succeeded in identifying more precisely, was photographed by us with sufficient clarity so that we could measure some zones for the purpose of determining wavelengths. The results of these measurements are set out in the table below and the wavelengths of the darker lines in the absorption spectrum of the bromine vapor according to Hasse 1 b e rg are entered.

Eder and Valenta light lines in the band emission spectrum of the bromine vapor i Hasselberg dark lines in the absorption spectrum of the bromine vapor

5593 · 38 1 5593 · 17

5592 99 1 5592 68

5592 47 1 5592 24

5592 05 1 5591 90

5591 19 1 5591 56

5590 86 5590 82 1 5591 10

5590 50 5590 52 2 5590 71

5590 20 5590 19 3 5590 38

5589 99 5589 97 4 5590 16

5589 67 5589 67 2 5589 84

5589 · 24 5589 · 49

5587 71 5589 05

1) Wiedemann: "Ann. •, 1883, vol. XIX, pag. 75.

2) Crowns: "About the Spectra of Iodine", Inaugural Dissertation, Kn 1897, p. 24.

A comparison of the two tables shows that the spectra are very similar. Some line groups, for example 5593 to 5589, are undoubtedly analogous, that is, the luminous lines of the band emission spectrum in P i c k e r's rings have one and the same wavelength as the dark lines the band absorption spectrum of bromine vapor.

Another group of lines shows only partial, but by no means perfect, identity of the wavelengths of the two types of band spectrum.

1 Eder and Valenta 1 light lines in the j band emission spectrum of. i bromine vapor 5516 91 5513 64 5512 79 5511 53 5511 08 5510 7] 5510 17 5509 79 5509 48 5509 06 5508 71 5508 21st'5507 80 5507 50  
5506 69 5506 21 5505 97 5505 60 5505 24 5504 51 5504 08 5503 86 5503 46 5503 36 some lines are missing 5501 59 5501 26 5500 82 5500 81 5496 61 5496 19 5495 71 5494 . 79 5494 . 30 5493 . 72 1 ;,  $\frac{1}{2}$   
 $\frac{1}{2}$  1  $\frac{1}{2}$  ',  $\frac{1}{2}$  ' /, 2 2 1 2 2 1 3 2  $\frac{1}{2}$  1 1 1 3 2 2 2 Hasselberg dark lines in the absorption spectrum des bromine vapor 5517 03 5513 73 5512 82 5511 65 5511 03 5510 69 5510 35 5509 87 5509 62 5509 06 5508 87 5508 21 5507 59 5506 88 5506 36 5505 98 5505 75 5505 11 5504 72 5504 31 5503 90 5503 23 5501 46 5501 13 5500 58 many lines 5496 41 5496 01 5495 53 5494 95 5494 30 5493 78 Note main line

The emission band spectrum of the Bromdarnpfes anticipated by P i c k e r and H i t t o r f is thus proven experimentally as existing by these findings.

The line spectrum, which we photographed from  $\lambda = 3900$  to  $\lambda = 3684$  with our large concave grating in the second order, and measured under the microscope, is more characteristic of the spectral detection of bromine. As a standard we calculated the R o w l a n d's iron lines with those values which R o w l a n d ascribed to them in the solar spectrum.

We took the photographs in the red and yellow spectral regions in the spectrum of the first order. The photographs of the bromine spectrum from  $\lambda = 6632$  to  $\lambda = 5180$  are of very satisfactory equality

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moderation. The recordings were made ... on silver-bromide gelatine drying plates, which we had made sensitive to the rays concerned by bathing in dye lungs. This is probably the first successful heliographic reproduction of this difficult-to-photograph area of low-light spectral phenomena in the less breakable part.

The determined wavelengths are compiled in the following table: Wavelength measurements in the spectrum of

bromine.

## Eder and Valenta Older Observations Eder and Valenta Older Observations

J. M. Eder and E. Valenta.

(Presented at the meeting of the Imperial Academy of Sciences on July 13, 1899.)

For orientation in the extreme ultraviolet, precisely determined spectrum photographs of metals, which give typical spectra, are of value. This applies to both the grating and the prismatic spectrum.

In spite of the fact that photographs of ultraviolet grating spectra have been published several times, little attention has been paid to the areas of the smallest wavelengths. First of all, we have in mind those short-celled spectral areas which can still be photographed without removing the atmospheric air from the path of light rays, without going into those areas which can only be seen in the vacuum spectrograph (after Sc human n: session area d . kais. acad.

d. Wissensch., Vol. CII, Abth. III a, July 1893) are detectable. The limit of the frangible ultraviolet spectrum that can be achieved by photographic means is, according to the unanimous statements made by Cornu 1), V. Schumann 2), Kayser and Runge 3) at approximately  $\lambda = 1850$  Angström units, but this region is already usually difficult to reach.

The limit of the achievable spectrum photographs in the extreme ultraviolet when using normal bromosilver gelatine drying plates depends on the absorption of the air layer through which the rays have to pass, on the prisms and lenses made of mountain crystal that may be present in the device and, finally, on the absorbing effect of the gelatine layer the drying plates.

These circumstances are so well known that no further explanation is required.

F Grating spectrographs of larger dispersion are missing until now clear and clear spectrum photographs in the most breakable ultraviolet, which would enable a reliable orientation in the spectral regions from  $\lambda = 2770$  to  $\lambda = 1999$ . The greater dispersion of such spectra is self-evident

1). Journal de Phys. ", 1881, Vol. X, p. 425; Kayser's «Textbook of Spectral Analysis», 1883, p. 231.

2) meeting area d. kais. acad. d. Wissensch., Vienna, mathem.-naturw. Cl.

3) Treatises d. kigl. prussia. Akad. D. Wissensch., Berlin 1892. 48

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in the case of very linear spectra, such as, for example, the arc and spark spectrum of iron, a great clarity of the photographic images.

It is well known that not all iron lines in the spark spectrum coincide with those of the arc, but many lines are missing now in one and now in the other spectrum and only appear after very long exposures with characteristically different intensities.

The comparative tables 1) of the lattice and arc spectrum of iron, first published by Liveing and De la Rue, prove this to be true of genes; However, it is difficult to relate these wavelengths reliably to the new standards of Rowland, because in these and all later publications dealing with the iron spectrum (by Kayser and Runge 2), Exner and Haschek 3) There are no comparative photographs of the sparks and arcs which have been brought to coincidence. Standard spectra which extend even further into the

ultraviolet and which are precisely oriented with regard to the wavelengths in arcs and sparks are also missing. We have tried to use our rangesen Concavgitters to create these aids, which are not unimportant for the spectral analyst. First of all, we took pictures of the iron spectrum in the sparks and arcs in a coining manner, which, however, caused some measurements in order to find exact coi "incidences and correct exposure times. Likewise, nickel and cobalt, as well as copper, were examined in the same way and their spectrum photographs in the enclosed Plates reproduced heliographically. The sight of the deviations of the two types of spectrum is highly instructive and interesting and does not require any further description. In such spectral photographs, the lines of the iron spectra are always particularly sharp, less those of the nickel and cobalt spectra, which is why we only use the iron spectrum as a standard. We have not only photographed these important iron standards, but also subjected them to an accurate wavelength measurement. The wavelengths in the iron spectrum determined by us on the basis of our own measurements and related to R o w 1an d's standard are given in the following table.

We consider the accuracy · f achieved by us to be good and estimate the possible error in our measurements within the limits  $\pm 0 \cdot 01$ ; perhaps even  $\pm 0.005$  on average. Our iron line standards given at the end of the treatise in connection with the illustration (Plate XXIV, Fig. 1) enable safe orientation in this area, both when working in arches and in sparks. The nickel spectrum is decidedly too bright against the short-wave ultraviolet than iron; Cobalt is in the middle 3). All three spectra were taken with moderately long exposures; with long exposures many more lines appear, the spectrum extends a little further into the ultraviolet, but the characteristic habitus in the structure of the spectra is then much more indistinct.

We have only entered a few wavelengths of the nickel spectrum, the cobalt spectrum is set below that, provided that an exact orientation is adhered to.

We have already stated earlier and shown 4) that the iron spectrum suddenly loses its brightness at), = 2327 and the lines that now follow, which are still numerous (). <2327) are relatively poor in light, if they can still be clearly detected even with longer exposure. Our spectrum photograph is deliberately made with a shorter exposure so that the most important area (A> 2327) appears clearly and distinctly; many faint lines still appear in ample exposure, but what is characteristic in the arrangement of the lines of the two kinds of the iron spectrum is blurred.

1) Watts: "Index of Spectra".

2) meeting area d. kais. Akad, d. Wissensch., Vienna, rnathern. natural CL, Vol. XVI, July 1897.

3) cf. p. 49 of these treatises.

4) cf. p. 50 of these treatises.

F the most breakable ultraviolet, which follows A = 2327, appears to us on the basis of numerous experiments the copper spectrum as the most suitable comparison spectrum; Its lines are, however, neither in the spark nor in the arc as sharp as those of the iron spectrum, but one finds a plentiful number of lines which are still sufficiently sharp, very evenly distributed from} = 2369 to} = 1999, even

up to 1944. As a result, we attached great importance to the precise determination of the copper spectrum (sparks and arcs) and produced photographs of the same at medium exposure in order to be able to show the main lines characteristically (grating spectrum

see Plate XXIV, Fig. 4, quartz spectrum see Plate XXVI, Fig. 1). The comparison of the spark spectrum with the arc spectrum of copper turns out to be very interesting (Plate XXIV, Fig. 4).

We have ensured the same thing by repeated measurements (by means of the microscope) of the spectrum photographs obtained with the large grating and referred to Row 1 on d's standards. The table below gives the result of these measurements with a probable error limit of  $\pm 0.01$  fear r m units. We note that we have already measured the copper spectrum very carefully with a small grating apparatus and with the quartz spectrograph. The comparison of the recently determined numbers with the earlier ones is therefore a fairly reliable measure of the performance of both types of observation, although the large grid provides more precise numbers.

The table at the end of this treatise contains the values we determined for our copper standards, on which we based the measurements on other elements (following the iron standards) from  $A = 2769$  to  $A = 1938$ .

The copper spectrum is also one of the most important comparative spectra for the prismatic (quartz) spectrum. \ i \ Tir have repeatedly pointed out that even the bright grating in the extreme ultraviolet is considerably behind the quartz spectrograph. It was possible to get the copper line), = 1999, by means of a grid, only after many hours of exposure, but in the quartz spectrograph easily with exposures of  $\frac{1}{4}$  to  $\frac{1}{4}$  hour under otherwise identical conditions. The neighboring copper lines  $A < 1970$  are only detectable in the grid with the largest measurement 1), but very lightly in the quartz spectrograph (see Plate XXIV, Fig. 4 and Plate XXVI, Fig. 1). With a grating spectrograph (in air) it is extremely difficult to penetrate into the extreme ultraviolet through prolonged exposure, because for a certain period of time the diffuse light which is always present in the spectrum (despite all precautionary measures) causes an ever-growing veil, which covers the weaker lines so that they can hardly be evoked. In this regard, working with the quartz spectrograph in the extreme ultraviolet is far more successful.

Very good standards for the extreme ultraviolet are provided by aluminum, the spectrum of which does not show a coherent system of lines, but has some very light lines in the region of  $A = 1850$ . These line groups were first measured by Co r n u 2) approximately in the prismatic spectrum, later by Runge 3) in the vacuum spectrograph with great accuracy between), = 1989 to), = 1854 fear r m units. In addition to the four already known lines, we found two sharp, new aluminum lines in this area in the quartz spectrograph, which we will request a little later in the table (based on the values found by Runge). In our photograph of the aluminum spectrum, in addition to the strong line  $A = 1935$ , a weaker, but nevertheless very clear and sharp line is noticeable, which we determined as  $A = 1930 \cdot 41$ . This line, as well as the line) = 1857, are new by us as aluminum lines.

1) Kayser and Runge came to  $Cu J. = 1943$ , Exner and Haschek to), =  $2105 \cdot 0$ .

2) «Journ. de Phys., 1881, Vol. X, p. 425.

3) «Astrophys. , foup1. », I 8951 vol. I, pag. 433. 48 \*

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It is noteworthy that the breakable component of the Cornu aluminum line  $1933 \cdot 5$

(according to our measurements the double line), = 1935, 1930) according to the information from V. Schumann's data

To tackle silicon. \ Vir therefore have first before we counter the shortwave spectral regions had made our studies, with the information Schumann's the line 1929 as the most breakable Silicon line included in our tables 1).

C. Leiss also writes ("Zeitschrift f Instrumentenkunde", 1898, p. 331): "The paler breakable component of the double line No. 31 according to Cornu (that is), = 1935, 1930 according to our measurements)

goes like Dr. V. Schumann was the first to be found, silicon, so it becomes pure aluminum to not give".

We applied our special line to this line in the new arrangement of our quartz spectrograph. Attention to and received the same with fairly pure aluminum, which is very small amounts, however contains at least 0.110, silicon, with the greatest possible clarity. When we cross-check the spark spectrum

of silicon-copper (with a content of at least  $10 \frac{1}{4}$  silicon) examined, we received despite twice as long exposure no trace of this line, but all the others determined by us

Silicon lines.

\ We are therefore able to use the previously frozen Schumann's called " $\lambda = 1929$ "

The silicon line should be deleted from the table of silicon and, for the time being, the aluminum spectrum to be classified.

At this point we note that we checked our measurements at that time and that the extremely sharp image with a greater dispersion than we had at that time, of the most breakable silicon line, the wavelength) =  $2124 \cdot 17$ . Our earlier number 2123, which was related to a less sharp photograph and more inaccurate standards, is to be replaced by the correct value above.

With reference to our iron and copper standards, as well as in the extreme ultraviolet on aluminum, we have also redefined the spark spectrum of gold, because it can be very useful for comparative images in the extreme ultraviolet. The gold spectrum, however, requires a significantly longer exposure time (2 to 3 times) than the copper spectrum. The table which gives our new measurements of the wavelengths obtained with the large grating and with the quartz apparatus is given a little later.

We have also given a heliographic picture of the most breakable ultraviolet gold spectrum (obtained by means of the quartz spectrograph) in Plate XXVI, Fig. 2.

Cadmium, zinc and lead (possibly the alloy of these three metals) also appear to be well suited for orientation in the extreme ultraviolet. However, the extensive broadening of many of these lines makes accurate measurements difficult; which is why these metals are very suitable for general orientation, but not as good as so-called standards for comparison appear with greater dispersion.

Good reproductions of the spectra of these elements, in the most frangible part, are not unimportant for the spectral analyst, which is why we shall tone the spark spectra of these three metals (photographs with short exposure), as well as those of thallium and tin (see Plate XXV, Figs. 4 and 5 ).

The three first-mentioned metal spectra (Cd, Zn, Pb) are made with pure material, the thallium contained a little lead, which is noted in the relevant figure, the tin was of unsatisfactory purity, which is why we have a number of foreign lines (Cu, Pb, Fe etc.) on the spectrum negative so that the image (Plate XXV, Fig. 5) is not free from retouching. This figure is therefore less reliable than the other heliographic spectrum figures on our panels.

1) Eder and Valenta: "On the emission spectrum of carbon and silicon", see p. 58 of these treatises; also Eder and Valenta: • The line spectrum of silicon, see p. 75 of these treatises,

Finally we give a heliographic reproduction of spark spectrum of calcium, which we photographed with the large grid 1). This shows the enormous differences in intensity in the spectrum of calcium. In order not to mix up the habitus of the calcium spark spectrum, we started with rather short exposures, nevertheless the group at  $\lambda = 3178$  to  $\lambda = 3169$  is already overexposed and unclear, so that especially this group on the accompanying table is not so correct appears as occasionally in our earlier detailed study of this subject 2). The reproduction of the other groups of lines has, however, been achieved with satisfactory clarity, and so this table may be taken as an appropriate addition to ours as well as to other treatises on the spectrum of calcium.

The use of the quartz spectrograph is, as mentioned, for the most breakable ultraviolet, namely  $\lambda < 2000$ , to be preferred to the grating because of the greater light intensity. In these spectral regions, even with the use of a single quartz prism of  $60^\circ$  and lenses of  $60^\circ$ , the dispersion is a respectable one and the field of view of the sharp spectral lines is extensive.

Nevertheless, the production of precise spectral photographs by means of the quartz apparatus in the districts  $\lambda = 2300$  to  $1854$ , presents undeniable difficulties as soon as the best definition of the most breakable lines is required. Since such spectral photographs with precisely oriented standards related to Row 1 and 2's No 1 ~ 10 spectra are important and have so far not been shown sufficiently clearly 3), we create a heliographic table with standards up to  $1850$  in the prismatic spectrum of copper, gold, Aluminum, cadmium and zinc.

The calculation of the wavelengths in the prismatic spectrum is far more complicated and less reliable than in the grating spectrum. The very important treatise by J. Hartmann: "About a simple interpolation formula for the prismatic spectrum" 4) in this case remedies the urgent need for practical spectrometry.

Hartmann set up the following simple interpolation formula to determine the wavelengths in the prismatic spectrum (with glass prisms):



In the same  $s$  means the direct measurement result, i.e. circular reading, scale parts, screw parts of anocular micrometer or linear quantities measured on the photographic plate:

1) In the addendum to our treatise, Eder and Valentia: "On the spark spectrum of calcium and lithium", see p. 333 of these treatises. The observations recorded there were referred to by Prof. J. Wilsing: "On the interpretation of the typical spectrum of the new stars", session b. d. kigl. p1 euss. Akad. D.Wissensch., Berlin 1899, Vol. XXIV, pag. 426.

2) Since calcium often appears as a contamination of other bodies, the view of the image of its sparkspectrum can also be used several times in this direction.

3) C. Leiss in his treatise on quartz spectrographs and newer optical spectrographic auxiliary apparatus ("Zeitschr. F Instrumentenlrnde", November 1898) with a much smaller dispersion than that with which we were working, fairly good collotype images of the spark spectra of zinc, Calcium, silver and aluminum. ] The aluminum spectrum from Leiss extends to  $\lambda = 1854$ , but the zinc spectrum is in its characteristic area in the extreme ultraviolet, that is in the group 2138 to 2025, hardly reproduced there, and also with cadmium and silver the more breakable part of the spectrum is little takes into account. Since Leiss was primarily about demonstrating the efficiency of the apparatus constructed in the Fues'schen Werkstätte in Steglitz, the entry was correcter, more harmonious, to Rowland's standardrelated wavelengths are not taken into account and are therefore the

a. a. 0. The wavelengths entered cannot be used for measurement purposes.

4) «Publications of the Astrophysical Laboratory in Potsdam», No. 42, Appendix to the XII. Gang, 1898,

.t. M. Eder and E. Valentia.

), 0 is a constant of the spectrograph, which is determined only once for each instrument;  $s_0$  is determined by the type of suitability of the plate in the measuring apparatus, so it is the zero point of the counting;  $C$  is the screw value of the micrometer screw or the scale of the measuring device, which is constant as long as one uses the same spectrograph and the same measuring device (apart from temperature corrections).

One did with a spectrographer. Taking the first spectrum and measuring it, it is necessary to know the wavelengths of three of the measured lines (standards) in order to immediately have the wavelengths of all the other lines 1). If  $\lambda_1, \lambda_2, \lambda_3$  are the wavelengths of the three standards to which the scale divisions  $s_1, s_2$  and  $s_3$  go, and if one uses these values to form the three equations according to Hartmann's interpolation formula, then the following list results for  $s_0, C$  and  $A_0$ :

$s_1 (\lambda_1, 1-A_0) (s_3-s_2) -ss (\lambda_2, 2-A_0) (s_2-s_1)$

So =

$(\lambda_1 - \lambda_2) (ss-s_2) - (\lambda_2 - \lambda_3) (s_2-s_1)$

\ Vir tried to find out whether this formula applies to the quartz spectrograph as well as that of Hartmann benzten glass prisms.

As a control we drew the resulting lines of the copper, aluminum and gold spectrum approached (see above) and tried whether the above formula for interpolation for this special case was. It turned out that, in fact, there are f small spectral regions of about 130 fearful Units the Hart man n formula gent.

We chose three normal lines for the calculation of a formula, namely the copper lines  $A_1 = 2126.09$ ,  $A_2 = 2037.25$  and  $A_3 = 1999.71$  (in our measuring apparatus the first line,  $s_1$ , at the scale divisions 50,000, the second,  $s_2$ , at  $75 \cdot 8945$  and the last,  $s_3$ , at  $87 \cdot 9915$ ) f the district delimited by them; f the neighboring spectrum but as standards the copper line),  $1 = 1999 \cdot 71$ , the aluminum lines \*),  $2 = 1835 \cdot 29$  and  $1-3 = 1862 \cdot 20$ , with the scale divisions  $s_1 = 87 \cdot 9915$ ,  $s_2 = 110 \cdot 8010$  and  $s_3 = 140 \cdot 2840$ ; f the district  $A = 2126$  bis),  $= 1999$  provided Hartmann's formula by inserting the

$$475980) \cdot = 303.00 + s + 309.750'$$

f the district 1999 to 1862 and the same zero point of the scale the formula  $422456) \cdot 72 + s + 287.529'$   
 $= 874$

The accuracy of the wavelengths calculated according to this formula in the prismatic spectrum was.  $\pm 0.06$  to (in the worst case)  $\pm 0.10$  Angstr's units, thus meeting the requirements of practical spectroscopy.

The tables below contain our re-determinations of the major standards of the ultraviolet spectrum of iron, copper, aluminum, gold, zinc, cadmium, lead, thallium, and antimony.

1) In later measurements it is sufficient, at least for the reliable identification of all lines, if one only knows the wavelength of a single line of the entire spectrum; from this only  $s$  (l 'while) (! and  $c$  are known from  $c$ ;! en other recordings.

1. Standards in the spark spectrum of iron from 'A = 3002 to' A =

2280. Spark spectrum from Eder and Valent a, based on R o w 1 an

d's standards 3002 796 1) 2883 825 2767 630 3)

2994 \cdot 547 3) 2873 \cdot 519 1) 2747 \cdot 077 3)

2985 \cdot 674 1) 2872 \cdot 504 1) 2746 \cdot 590 ")

2984 965 2) 2835 840 1) 2743 311 2)

2973 · 315 4) 2823.418 4) 2720 · 99 4)

2967. 016 4) 2794 · 016 1) 2706 · 684 ")

2937 · 020 3) 2788.236 4) 2704 · 112 1)

2926 692 1)

2692 721 1) 2599 494 3) 2689 30 2598 460 3) 2684 871 1) '!' 585 963 3) 2666 745 5) 2582 673 3) 2664

770 1) 2563 569 3 ) 2628 387 3) 2534 47 4) 2611 965 3) 2533 70 4) 2493 30 2) 2375 318 2454 62 ') 2373

844 3) 2439 37') 2364 91 2413 39 3) 2338 · 108 2406 · 743 ") 2332 · 880 3) 2399 · 328 3) 2327 · 484 3)

2388 · 710") 2280 · 00 ')

1) Clear and strong in the spark, but not in the arc.

2) Weaker in the arc than in the spark. ") Clearly both in the arc and in the spark.

4) Stronger in the arc than in the spark, but also clear and sharp in the latter.

5) This line in the spark does not coincide with the nearby Fe line of the arc.

II. Complete spectrum of sparks and arcs of copper from), = 2769 to), = 1938.

A 1 i Bogenspectrum Kayser and Runge Comment1 1 1 A 1 i Funkenspectrum Eder and ValentaCommenti

2769 · 37 2768 · 94 2766 · 50 -2751 · 86 1 1 4 5 -1 widened reverse widened - 1 2769 · 89 -2766 · 47 2763

· 80 2751 · 33 1 1 i 1 8 -2 1 2 sharp 1 i 1 1 "" widened

In addition, the third-order copper lines  $t = 3247 \cdot 671$  and  $3274 \cdot 090$  (Rowland) came in the arc spectrum in the same field of view, which always appear reversed in the arc (symmetrically broadened), while the arc spectrum of the iron photographed as normal contained a trace of copper and there was a fine, black copper line, which with the reverse appearance completely coincided (1).

Our heliographic Plate XIX, Fig. II, Spectra 1 and 2, shows the exact spectrum photograph of the arc spectrum of a Zipk copper alloy; one sees how, with increasing exposure, all the lines of the arc spectrum remain fairly sharp and widen symmetrically. In the spark spectrum, pure zinc gives the lines}

= 4680, 4722, 4810 with increasing exposure on one side, strongly broadened according to Roth; with precise minimum exposure, however, the brightest part of the line in the strongest bottle spark appears sufficiently sharp to be able to determine its length exactly and to be able to ensure the coincidence with the arc 1 under the microscope, which can also be seen from our table (Fig. II, Spectra 1 to 4). In the zinc lines  $A = 3282, 3302, 3345 \cdot 1$  we also always found complete coincidence in the arc lines and spark lines; the zinc spark lines  $A = 3345 \cdot 1$  and  $3302 \cdot 7$  reverse very easily and then coincide vlig with the (not reversed) arc line. In overexposure, these lines widen towards ultraviolet. The zinc line  $t = 3345$

· 698 and  $3303 \cdot 068$ , which can be kept sharp and fine both in the spark and in the arc without difficulty, is described by Hasche k itself not as displaceable, because its tendency to remain sharp even with

imprecise exposure times protects against those deceptions which can occur with the unilaterally widening lines  $\lambda = 4680, 4722$  etc. if the definition is inadequate.

FIG. III shows the spark spectrum of pure zinc in spectrum 1 and 3; Spectrum 2 in the middle is the arc spectrum of the zinc-copper alloy and it all three extends the arc spectrum of an iron wire containing traces of copper. One sees the precise coincidence of the inverted copper arc line  $\lambda = 3247$  and  $3274$  with the copper spark line that is not inverted. The zinc lines  $\lambda = 4722$  and  $4810$  (Fig. JII) are somewhat abundantly exposed and developed to a strong blackening, whereby the arc lines of the middle spectrum have widened fairly evenly on both sides, while the spark lines show unilateral broadening and in their course the beginning of apparent shifts, which disappears with minimal exposure and shorter development, after which the complete coincidence analogously to FIG. II is undoubtedly visible.

The zinc lines),  $\lambda = 3345$  and  $3302$  of Fig. III also show that these zinc lines in the spark are by no means shifted towards the arc line to the side of the greater wavelength, as Haschek (op. Cit.) Erroneously states. This can be seen even more clearly when measuring the original negatives under the microscope of the measuring device.

1) In agreement with our experiments, Exner and Haschek also postulate the two copper lines  $3247$  and  $3274$  in their "Wavelength Tables", Vol. I, p. 21, as immovable.

J. M. Eder and E. Valenta.

The presumption that Haschek had poorly defined spectra is increased by the fact that the named missed the finer construction of some zinc spark lines, which is very peculiar. While Haschek did not escape the asymmetrically very strong broadening of the zinc lines  $\lambda = 4680, 4722, 4810$  according to Roth, he did not notice that the zinc lines  $\lambda = 3345 \cdot 1$  and  $3302 \cdot 7$  show a tendency to widen slightly towards the shorter wavelength side and as a result give them the tendency to seem "displacements" against Roth. Nevertheless, Haschek finds these lines in the spark particularly strongly shifted towards Roth (compared to Bogen), and on the contrary we find that with a correct short exposition there is no shift at all, but coincidence.

After we could not confirm the quoted statement of the line shift in the spark against the same lines in the arc, further attempts were made to investigate the influence of the partial pressure of the luminous zinc vapor on the "shift" of the spectrum lines. For this purpose we subjected the spark spectrum of pure zinc and that of alloys of  $1\frac{1}{4}$  zinc + 99% lead, as well as that of  $50\frac{1}{4}$  zinc +  $50\frac{1}{4}$  lead, and also alloys of  $36 \cdot 9\%$  zinc +  $63 \cdot 1\frac{1}{4}\%$  copper to a detailed investigation.

In the case of alloys that are poor in zinc, according to the long-published, well-known and never disputed experience of all spectral analysts, and this applies to all spectra, especially those with asymmetrically broadened lines, all those lines, even with increasing exposure, which reach zinc, remain fairly sharp. Alloys, however, show the tendency towards one-sided broadening to a high degree; to this extent the influence of the partial pressure on the width of the spectral lines undoubtedly asserts itself.

As the exposure time increases, the one-sided widening phenomena in low-zinc and high-zinc alloys do not run parallel; one therefore measures on the stronger exposure plates change the wavelength of low-zinc and high-zinc alloys by adjusting them to the center of the not well-defined lines, then apparent line shifts occur with increasing partial pressures (analogous to the figure in Fig. Exposure times returns and has achieved well-defined spectra.

· A 1 ¼ zinc alloy (1 ¼ zinc + 99 ¼ lead) naturally gives the individual zinc lines in the spark less brightly than a zinc-rich zinc alloy, for example a 50 ¼ zinc alloy. A preliminary test for our strongest bottle spark (Ruhmkorff) showed that the low-zinc alloy (1 ¼ ¼ ") must be exposed to the zinc lines A = 4680, 4722, 4810 for around 15 minutes compared with the zinc-rich (50 ¼ ") alloy for about 15 minutes with both alloys approximately equally strong (equally bright) on the photographic plate. According to this, in our preliminary tests, the zinc lines in the former case would be about 30 times brighter than in the latter case.

If one uses the equivalent exposure time and approaches the minimum exposure time, which in both n cases still gives measurable weak lines in the spectrogram, the wavelengths of the zinc lines in the spark spectrum are = 4680 · 327, 4722 · 333 and 4810 · 719 at 1¼ , with 4¼, with 50¼ zinc alloy and with pure zinc exactly the same, and we could never (not even in the strongest bottle spark) observe the Ex ner- Mache'schen, respectively Haschek'sche "line shifts".

Hasche k 1) states that alloys with little zinc (4¼ zinc) give zinc lines in the spark spectrum of wavelength A = 4722 · 399, with 50¼ zinc but 4722 · 434, which would be a considerable shift according to Roth with increasing partial pressure; he finds zinc line 4680 in low-zinc alloys (4¼ zinc) too weak to be able to measure it. But you can use this line 4680 in

1) «Meeting area. d. kais. acad. d. Wiss. », Vienna, February 1902, Vol. CXI, Abth. II a, p. 238 and 240.

•

Immutability of the wavelengths in the spark and arc spectrum of zinc.

even 1¼ alloys can be measured (this is clearly shown by our table, Fig. IV, spectrum 4) if the correct exposure time is chosen. Apparently, Hasche k under-exposed the low-zinc alloy, e-exposed the high- zinc alloy and, as a result of a deception, was subject to unilateral broadening of the lines and poor definition of his spectra. As far as we can see, Hasche k supports his displacement theory with only unilaterally broadened lines; with the sharp ones there is not even an apparent shift of the lines of the spark spectrum against the arc spectrum.

So our results are:

1. In the spark spectrum of the zinc there are no shifts of measurable magnitude with respect to the lines of the arc spectrum;
2. the quantity of the element present or the partial pressure of its vapor does not result in a shift in the lines of the spark spectrum and thus Haschek's system of quantitative spectral analysis has also become obsolete, whereas those conclusions are those which presuppose the constancy of the spectral lines (shifts of the spectral lines in the vision radius after the Dopp 1 see principles, etc.) and which would have appeared doubtful due to Haschek's reasoning, according to our observations, all the more securely founded.

## Contributions to photochemistry and spectral analysis

### Part III. Behavior of Silver Salts Against the Spectrum Color Sensitizers

I.

#### BEHAVIOR OF SILVER SALTS TO SPECTRUM (COLOR SENSITIZERS).

About the behavior of the haloid connections

of silver against the solar spectrum and the increase in its sensitivity through dyes. Of

Per Meskicder:

(Submitted at the meeting of the Imperial Academy of Sciences on December 4, 1840.) -

The effect of the solar spectrum on silver salts was first studied by Scheele<sup>1)</sup> 1777, then Senebier<sup>2)</sup> 1782 with chlorine silver, whereupon the discovery of chemically acting ultraviolet rays by Ritter<sup>3)</sup> And almost simultaneously by Wollaston<sup>4)</sup>, also with chlorine silver, happened in 1801. Herschel<sup>5)</sup> Examined the behavior of various silver and iron salts, flower pigments, etc. in the spectrum (1840) without having received Fraunhofer lines. This first photographed Becquerel<sup>6)</sup> in the years 1842 and 1843. Becquerel as well as Draper<sup>7)</sup> (1843) mainly worked with daguerreotype plates, by means of which the latter also discovered the infrared rays.

Crookes<sup>8)</sup> first investigated the action of the solar spectrum on iodized silver and bromide silver in the wet Collodion process with acidic pyrogallol and iron vitriol production in 1853 and 1854. He was followed by J. Müller<sup>9)</sup> (1856), Helmholtz<sup>10)</sup> (1857), and more recently by Rutherford, Mascart, BacNosel, CGornu. ur. n.

While the named usually the most complete possible representation of the lines in the solar spectrum intended, Schultz-Sellak<sup>11)</sup>, H.W. Vogel<sup>12)</sup> And Abney<sup>13)</sup> their attention

1) Scheele: "Aeris atque ignis examen chemicum", Upsala 1777, p. 62; German: "Chemical treatise of the air and fire", 1st ed. 1777; 2nd edition 1782.

2) Senebier: "Mémoires physico-chimiques sur l'influence de la lumière solaire pour modifier les êtres des trois règnes de la nature", Genève 1782.

3) First published on February 22nd, 1801 in the "Intellectivenblatt der Erlanger Literatur-Zeitung".

4), Philosophical Transact., 1802, p. 379. 5) "Gilbert's Annalen, Vol. XXI, p. 416 and Vol. XXXIX, p. 291. 6)

7) These and the above-mentioned treatises are excerpted from Eder's "History of Photochemistry" (Photographische Correspondenz, 1881 and ff.).

- 5) Philosophical Transact., 1840 and 1841 and Lond. Edinb. and Dubl. Philos. Journ., 1843, Art. XIX, pag.44.
- 6) Biblioth. univers. de Geneve, 1842, vol. XL. Also Becquerel: "La Lumiere", 1867, vol. I, p. 138.
- 7) philosopher. Magazine (3), Vol. XXI, p. 360.
- 8) Journ. Photogr. Society, London 1853, Vol. I, pp. 77 and 98; 1854, Vol. II, p. 293; Poggend: Annal., Vol.IIIC, pag. 616.
- “) Poggend: Annal., Vol. IIIC, pag. 139.
- 10) Negotiations in nature. Assembly, Rheinl. 1859, 5. 17, based on Kreutzer's Annual Report for Photographers, 1857, p. 328.
- 11) reports d. German. chem. Gesellsch., Vol. IV, pag. 210 => u. ff.
- 12) Poggend: Annal., Vol. CLIIIN, pag. 223 and the later years; further reports d. German. chem.Gesellsch., 1874 and fi. Vol.
- 13) Photographic News, 1882, p. 181 and following to the London Royal Society. Proc.I

Dr | I. M. Eder.

on the sensitivity of various silver compounds in the wet and dry Collodion process to the spectrum and the latter two, as well as Schumann!), extended their observations to include bromosilver gelatin emulsions. However, since there are contradictions in the statements of the last three and the silver emulsions in gelatine ("gelatine dry plates") still exist in many respects little studied, so did I investigate more closely?).

In these investigations, which aim at the sensitivity of different silver compounds to rays of different wavelengths and to determine the maximum effect, the nature of the spectrograph is of great importance. Depending on the permeability of the prisms and lenses, the maximum effect shifts significantly, as does the expansion against ultraviolet.

Since Stokes had already found around 1852 (by means of fluorescent substances) that quartz allows the most ultraviolet through, Crookes used it for his work as early as 1854 (op. Cit.). He used two rock crystal prisms with a refractive angle of  $55^{\circ}$ , which were cut in such a way that the rays penetrated the rock crystal in the position at the minimum of deflection parallel to the optical axis, i.e. they were cut perpendicular to the axis. Fig. 1 shows the sketch of the Crookes apparatus. A is an adjustable gap; B the collimator lens, Z and E the prisms that can be moved at F, O the photographic camera. The photosensitive plate was at MN. With GKT and POR, the individual parts can be moved.

1) Photographisches Wochenblatt, 1882, 1883 and ff. Vol.

2?) As preliminary information on this subject, the following notes appeared in Photographische Correspondenz, year 1884, on p. 95:

À € œTry the great Steinheilâ €™ s Spectrogr

Aphen with bromine and iodine bromine plates gave some results about which I am making preliminary reports: iodine bromine silver, whereby iodine and bromine silver is emulsified and digested together, is more sensitive to the green and yellow rays than pure bromine silver. A mixture of 1 mol. Iodized silver to 8-20 mol. Bromide silver is very color-sensitive.

Dyes can act as optical sensitizers in different ways, depending on whether the bromosilver gelatine plates bathed in their solutions are exposed in the wet state or after drying. For example, fluorescein with soda strongly sensitizes to light green to yellow-green rays and gives a dark band, but little when dry. Acid fuchsin and bleu fluorescent sensitize for blue rays. Eosin by itself has little effect; with ammonia, however, there is a strong increase in yellow and yellow-green both wet and dry, and this applies not only to bromeosine, which Attout and Clayton was privileged in France, but also to iodeosine, which has not yet been tried and perhaps the same property shows even more strongly.

Braun in Dornach brings Collodion (wet process) on the market, which allows to photograph colored pictures in the correct reproduction of the light effect of blue and yellow and which seems to be colored with eosin. Hemp stalks in Munich are said to use a similar method for photographing the oil paintings. Prof. H. W. Vogel kindly sent us a photograph of a colored picture (yellow, blue, gold), which makes the yellow lighter than blue in an excellent way. This process is an enormous advance for the photography of colored objects. "

also p. 120:

"The other types of eosin on the market also gave results similar to bromine and iodeosine in ammoniacal solution. |

The increase in sensitivity through eosin, fluorescein etc. for spectral yellow, respectively green, is achieved not only with bromine and bromine iodine, but also with chlorine silver and its mixtures with iodine silver etc. in the form of gelatin emulsion.

Chloride of silver emulsion gives two maxima of the spectral effect: one for silver chlorine, the other for silver iodine. This occurs when both emulsions are prepared separately and then mixed. But even if silver nitrate is added to a mixture of iodine and potassium chloride and digested with ammonia or boiled, the maxima almost always remain (each for itself) without quickly equalizing, as with iodobromide silver. |

Silver chloroiodine gelatine with ammoniacal eosin is relatively much more sensitive to yellow than silver iodobromide; the former shows three maxima: one for chlorine silver in the extreme violet, one for iodized silver in indigo (G), one, and indeed the most intense, for eosin in yellow. â € "Since the light reflected by green leaves consists mainly of yellow, orange and light green (according to Reinke, this reflected light consists of rays in the red [before B] and those between C and E [Photographic News, 1884 , pag. 237; also Chemisches Centralblatt, 1884]) and dark green and blue are only weakly represented, then such plates would perhaps be very useful for landscape photographs. They can be



developed with ordinary iron oxalate with the addition of potassium bromide. The sensitivity of such plates to white light is 10-20 times less than that of conventional silver bromide gelatine plates.

About the behavior of the haloid connections etc. 3

Kalkspath (Icelandic spathe), which Mascart used when he photographed the solar spectrum up to 7 with a Norbert diffraction grating using calcareous prisms, is also considered to be very transparent to ultraviolet. Hughins photographed the spectra of the stars with a calcareous prism and two quartz lenses. Cornu initially designed a similar device

but his tablet about the ultraviolet cal.

Solar spectrum after recordings with quartz prisms, which were cemented together from two halves of right and left rotating quartz with a refractive angle of  $40^\circ$  each).

The influence of the substance of the prism on the expansion of the spectrum as well as the position of the maximum of the effect on silver bromide gelatine plates is assumed

Fig. 2 clearly shows. The same signed

Br SE,N

I after the engineer Schu-Crookes's Spectrograph.

man in Leipzig with great care: " - ae t great care he (facsimile after the original woodcuts.)

provided and not yet published comparative recordings of the solar spectrum by means of a spectrograph with quartz-calcite

Lenses and various prisms of  $60^\circ$ . The length of the spectra and the distance between the women Hofer's lines in FIG. 2 show the different FIG.

called the dispersion of prisms made of quartz, lime-quartz-calcite -

objective. late, heavy flint and light flint glass. The Er- ee a 6 F

elevation of the Curve represents the intensity of the

photographic image and the position of the maximum ROPONM HG F an â

€ œ = aeffect on bromosilver gelatine.

2 b>. M! In the middle of the quartz prism \*) you get a "rFreees Â £" light flint glass.

Spectrum to over R (an ultraviolet after Cornu's name); with calcareous sparÂ °?) extends in Ser  
â € œâ € œheavy flint glass. the same exposure, the effect is not so far into the effect of that  
produced by means of different prisms

Ultraviolet, namely to over?; with heavy flint sun spectrums on bromide silver gelatine.

1) Compt. rend., 1864, vol. LVII, pag. 111; Annal. Scient. de l'École Norm., 1864; Becquerel: "La Lumière", 1868, vol. I, p. 140; Schellen: "Spectral analysis", 1883, p. 426.

2) Compt. rend., Vol. XCI, p. 70.

3) Cornu: "Sur le specter normal du soleil, partie ultraviolette", 1882 (Ganthiers-Villars, Paris), in which the apparatus is described in detail. Also see Cornu's treatises: Annal. de l'école norm., 1874 (2), vol. III, p. 421; Arch. Des sc. Phys. Et nat. (2), Vol. LIII (1876), pag. 50; Compt. rend., 1878, p. 101; Supplement to d. Annal. Phys. Chem., 1878, VIII. 339.

4) A simple quartz prism, cut perpendicular to the axis, doubled the lines of the spectrum in Herr Schumann's investigations, despite the fact that the rays had the theoretically correct course, as mentioned above in Crookes' apparatus. The evil that is a consequence of the birefringence can be eliminated not only according to Cornu's method by cementing a right and a left turning prism, but also according to Schumann's communication by two separate quartz prisms of  $60^\circ$  each, one of which is clockwise and the other is cut from left-turning quartz perpendicular to the axis. The dispersion is then approximately the same as with a calcite prism, but the expansion towards the more breakable side is greater. Schumann found no difference between biconvex and planconvex lenses in the spectrograph, while Cornu prescribes planconvex. The quartz lenses require a very significant inclination of the plate to the pipe axis of the camera, namely 22-24 °%. However, Schumann succeeded in eliminating this by masking  $2\frac{1}{3}$  dm; in this case the plate can be perpendicular to the pipe axis, but the loss of light is significant.

5) The spectrum with a calcareous prism (cut perpendicular to the axis) showed the Fraunhofer lines in Mr. Schumann's photographic recordings completely sharp; with two or more, in spite of all care, he could not get a clear Spectra. The beautiful groups of lines in the ultraviolet then partly looked like twisted column shafts.

E \*

A J. M. Eder.

In glass, the effect does not even reach the limit of the visible violet, namely up to half the distance from HM to G; with light flint glass, on the other hand, up to N in ultraviolet. In the case of quartz and calcite, the maximum effect was closer to G, and in the case of glass more towards F.

Schumann also found river path, which Cornu used with quartz to make achromatized lenses to photograph the ultraviolet spectrum, very permeable to ultraviolet.

However, on the basis of his detailed experiments, Herr Schumann informs me that he prefers simple quartz lenses instead of achromatic quartz-calcite lenses for photographing the spectrum where there is a clear definition of lines. The lenses shouldn't be cemented for such purposes because Canada balsam swallows ultraviolet.

How damaging even very thin glass vessels are for studying the ultraviolet spectrum is shown by Mr. Schumann's experiments, in which a glass cover plate of 0.125 mm thickness already has a third of the external ultraviolet rays of the magnesium spark (over

- 277) swallowed; this result

Mes. is for the photography of Glasspectra  
relevant by means of suitable Geissler's  
tubes.

During my spectrographic experiments, a "large spectrograph" from Dr.  
Steinheil in Munich at bid, as well as a small one

Spectrograph with prisms & vision direct, also from Steinheil. The procurement of these  
two instruments was carried out by a k. k. Ministry of Cultus and Education enables subsidy  
granted.

The manufacturing process was based on my information and Dr. Steinheil had the optical con-  
periences carried out.

In Fig. 3 the large spectrograph is shown on the average. The light, which first passes the slit  
slide A, which is adjustable at O, in the focal point of the objective B, falls on the three prisms C,  
D and E, which all consist of a light flint glass and have a refractive angle of  $90^\circ$ . The resulting  
spectrum is projected by a photographic objective F onto plane G at the end of the camera H,  
where it can be photographed.

The objective of the slit telescope has an aperture of 34 mm and 325 mm focal length, while the  
photographic aplanatic objective F has 54 mm aperture and 600 mm focal length. The lenses  
are composed of such types of glass which absorb as little blue to ultraviolet rays as possible,  
which is why a great brightness is obtained in the blue and violet parts.

The refractive power of the prisms is for the lines:

1 Be Re eo 505) a ler ne  
ng. Their opening is 47  
mm.

With the spectrum, a scale can be photographed at the same time, which is  
enlarged by the photographic objective N and reflected on the last prism surface,  
also on the plane of the

About the behavior of the haloid connections etc. 5

photosensitive plate is thrown. K is a so-called guillotine moment lock to be able to expose  
quickly enough when working with direct sunlight. The two screws ZL and M are used to adjust  
the slit telescope in order to bring them into the center of the plate and to the minimum of the  
prism deflection when photographing special parts of the spectrum. With P and O the plane of  
the photosensitive plate can be inclined. It should also be noted that the slit slide of my  
apparatus allows an exact setting of the gap opening to  $\frac{1}{2}$ , .. mm; the edges of the gap are made  
of platinum and a micrometer screw conveys their movement. - The aperture of 0.02 mm  
gave the Fraunhofer lines very good sharpness; I seldom worked with a slit of  $0.04 \pm 0.01$  mm, which means that the lines are a lot Lose focus.

4 shows the external view of the spectrograph. In the case of the "most edler" gap, "which" of the lens: can be approached or removed from it via the center of the drive O.

The slide K (guillotine moment shutter) has a round opening inside and can be quickly pulled past by a spiral spring so that momentary exposure takes place; however, the slide can also be kept open for any length of time by means of a locking device.

L and M allow the slit telescope to be moved and its inclination to the prisms to be changed.

There are three prisms inside the brass body. N contains the comparison scale; F is the photographic object, 7 the Tlölz camera!

At R the cassette with the sensitive disk is inserted; on the 12 and 16 cm side length disc located in such a cassette can by shifting

three spectra can be recorded one after the other. SS are diaphragms (sliders made of blackened brass), to cut off sections as required.

Steinheil's large spectrograph.

The whole instrument is balanced by means of the weights ZT and can be rotated by means of the screws U and V without shaking after the "Sonnel". The use of a heliostat, which always changes in the quality of the light caused by sunlight?, is thereby bypassed.

Biel: range "of the 'spectrum, which? This' apparatus covers from the Fraunhofer line A to N 12 cm; beyond N the ultraviolet could no longer be photographed well because the absorption of the rays, their wavelength below 350 nm was too large. The lines of the spectrum are very sharp and well defined. The duration of the exposure of course varies significantly with the sensitivity of the specimens.

!) The splitting slide described is patented in Germany (German Reich patent no. 17092).

2) Silver mirrors reflect only the less breakable rays but cancel out the ultraviolet ones; Platinum, on the other hand, gives an excellent mirror for ultraviolet in layers which are still completely transparent (De Chardonnet, CorRnUu):

6 eNBerrdier

On bromide-silver gelatine plates, exposure to direct sunlight and a slit of 0.04 mm "momentarily" (ie about  $1/100$  s, second) up to 1 second; plates dyed with eosin dyes needed a 2-4 times, with cyanine a somewhat longer, plates colored with iodine green, methyl violet etc. even a 10-160 times longer exposure as soon as the light effect in the red (respectively yellow) 2 veileshervontsss should come into the Berzdieser long exposure In many cases the blue and violet rays have an enormously strong effect, which is caused by the lateral extension of the light effect

and haze. If you aim the spectral apparatus at the

Fig. 9. blue sky or clouds, you never get such sharp lines

A than in sunlight; very good optical sensitizers do then also their effect (e.g. eosin), weak

(e.g. most green dyes) but often show so little effect that it can easily be overlooked.

The little spectrograph was one of them

igen changes after H.W. Vogel's information?) Constructed; a spectroscope a vision directe is attached in front of a camera and the spectrum image is drawn (without the aid of a photographic objective) on the wet pane.

In Fig. 5 my little Spectrograph (von-Dr: Steinheil) is shown. A cylindrical converging lens A is attached in front of the slit B, which concentrates the light on the slit. Objective C of the slit telescope has a focal length of 81 mm. The prism set a vision directe consists of three crown glass prisms D (in the middle of the set, as well as the top and bottom) with a refracting angle of  $100^{\circ} 20'$  and two flint glass prisms cemented in between of  $105^{\circ} 00'$  (breaking angle \*); the dispersion from D to F is equal to  $4^{\circ} 6'$ , so for the entire spectrum A to F about  $15^{\circ}$ . The spectrum is photographed in the camera F; at G is the sensitive plate, which can be shifted small in a slide cassette. The screw E enables the spectroscope to be moved to focus the lines.

Such an instrument gives almost no spectrum from ultraviolet at all, but little beyond F; it is easier to use than the large spectrograph, but gives less clear spectra.

The influence of both instruments on the distribution of the chemical action of the solar spectrum is very important. The in the Spectro

graph & vision directe combined crown flint glass prisms

even the visible violet very much, as can be seen from FIG. 2; as a result of this, a small 'Spectrograph, the effect of the solar spectrum obtained with it on bromine-silver and chlorosilver gelatine emulsion on violet is strikingly reduced. At the

This is most pronounced with chlorosilver gelatine (with iron citrate developer), which in the large spectrograph with flint glass prisms shows the maximum of the effect at F at the beginning of the ultraviolet (Fig. 6, Curve 1; - the "dotted" line indicates the result with shorter exposure on), while in the small

Spectrographs (à vision directe) the maximum lies between G and F (Fig. 6, Curve 2). The Ver-

t) E.g. eosin plates take 1–5 seconds of exposure, iodine green plates 1–3 minutes.

2) For a detailed description, see Eder's "Detailed Handbook of Photography", Halle 1884, Vol. I, p. 42; also see: "Spectral analysis", 1883, p. 440.

\*) The refractive power of the flint glass of the prisms is for  $n_D = 1.6533$ ,  $n_F =$

1.6669. #, The refractive power of the crown glass of the prisms is for  $n_D =$

1.5107,  $n_F = 1.5168$ . About the behavior of the haloid connections. 2%

The difference between the two curves, as shown in "Fig. 6", is so great that you can hardly believe that you are looking at the same silver salt.

In. In my large spectral apparatus even the maximum of the effect is noticeably shifted, depending on whether the outer violet or blue-green is brought into the center of the field of vision. The assessment of various modifications of bromine and chlorine silver according to the maximum sensitivity is therefore an uncertain and only of relative value!).

It is all the more striking that the maxima of the sensitizing effects of dyes in red, yellow and green are so

act energetically that they (as far as my

Observations are sufficient) in each apparatus

At the same point, however, 1 spectrum image appears on each curve on chlorosilver gelatine with the large spectrograph. â€"Curve 2. The same with the small A vision spectrograph

after the light distribution more or less as it is:

intensive. My experiments below were eliminated with the large Steinheil

Spectrograph and are therefore all comparable with each other.

A. Silver bromide in the form of gelatin emulsion.

If you mix silver nitrate solution with excess bromammonium in the presence of gelatine (in red light), "finely divided powdery silver bromide" forms, which appears red when viewed through. Panels coated and dried with this emulsion?) Show an effect after brief exposure to the solar spectrum and development with iron oxalate \*) or alkaline pyrogallol?)

from purple to blue-green (7 to close to F) with the maximum effect of G /, FÂ®). For longer

%) For example, the division of bromide silver according to Prof. HW Vogel into blue-sensitive and indigo-sensitive (reports from the German chem. Society, 1881, vol. XIV, pag. 1024), which incidentally does not emerge from Abney's work (Proced. Royal. Soc., 1881, pag. 217; Photographic News, 1882).

2) See my treatise "Photochemie des Bromsilbers" (LXXXI. Vol. Der Sitzungsber. D. Imperial Akad. D. Wissensch. In Vienna, II. Abth., April issue 1880; also monthly issue for chemistry, 1880).

3) The following procedure proves to be practical for the production of this emulsion: 30 g of silver nitrate are in 250 cm<sup>3</sup> Dissolve water and add enough ammonia until the precipitate formed at the beginning dissolves again clearly. A. On the other hand, 20 g of bromammonium and 30-45 g of gelatine ("hard gelatine for emulsions" from the gelatine factory in Winterthur) are dissolved in the heat and the two solutions are then mixed at 30-35 ° C. by adding the silver solution is added to the bromine salt solution in small portions and shaken vigorously. The emulsion is then poured into a shallow bowl (which is in cold water), cut into small pieces after it has solidified and washed with water. â€"For more

steps and details, see Eder's "Theory and Practice of Photography with Silver Bromide Gelatine", Vienna 1881, as well as his "Detailed Handbook of Photography" (Volume VIII: "Photography with Silver Bromide Gelatine").

#) 1 vol. Cold, saturated iron vitriol solution, 4 vol. Cold, saturated, neutral potassium oxalate solution (for details see Eder's "Photography with bromosilver gelatine", op. Cit.).

5) The glycerine-pyrogallol developer is recommended as a good developer: Prepare two storage solutions: A: 10 g pyrogallol, 10 g glycerine in 100 cm<sup>3</sup> dissolved in strong alcohol; the mixture will last a few months. W: 20 cm<sup>3</sup> Ammonia (d = 0.91), 10 g glycerine, 6 g bromammonium and 100 cm<sup>3</sup> Water are mixed. Do you mix 100 cm<sup>3</sup> immediately before use? Water, 3 cm<sup>3</sup> of solution A, 4 cm<sup>3</sup> Solution B. If you want more clarity and contrast, you can still add 1 cm<sup>3</sup> Add bromammonium (1:10); the intensity of the image increases if you only use half of the water in the above procedure.

The potash developer also corresponds very well: A: 90g of pure potassium carbonate and 25g of neutral sodium sulfite are in 200 cm<sup>3</sup> Dissolved water; B: 12g pyrogallol, 1g citric acid, 25 g sodium sulfite are in 100 cm<sup>3</sup> Dissolved in water. Before use, mix 100 cm<sup>3</sup> Water, 2-3 cm<sup>3</sup> of solution A and 2 cm<sup>3</sup> the solution B. Before fixing, it is advisable to soak the plates in a concentrated alum solution for a few minutes, which will make the yellowish color of the matrices disappear.

6) That means a third of the distance from G

to F.3 Per Made

Exposure progresses the effect on both sides (up to Mrund-). The curve 3, Fig. 7 'shows: Picture of the intensity relationships of the effect of the spectrum, related to the Fraunhofer lines (the dotted Line the blackening after a short exposure, the full line after a long exposure).

If the ammoniacal emulsion mentioned above is digested at 30-40 ° C. by half a

Hour, or boil it for half an hour if the ammonia was left out and the reaction was acidic

Hour, so the bromide silver changes into the "finely divided-grain modification"; the grain of the bromosilver increases in size, allows blue light to pass through in a thin layer and the overall sensitivity to white light increases, which was described in my earlier treatise (a. a. ©.). At the same time, the sensitivity to violet and green advances in the spectrum; the maximum of the sensitivity in Fig. 7 goes a little further towards F (G', F). The N M EN, 6 F E De ah effect no longer appears so intense between Gand F; the curve of the

Spectral effect flattens out and

3 ||| stretches one- | with prolonged exposure | Bene en on the one hand to N, on the other hand to D and above \_â in \ | \* beyond (Curve 4 with short and long exposure). See ee peer Æ¶

With a diversion 3-10 times longer than to achieve the  
aforementioned.6 result is necessary, is approaching

7. "changes - the" curve of the 'Speetralwar- kung. It flattens out more and more,

the bromide of decomposition; at the same time there is no clearly recognizable maximum);

The photographic image lacks intensity. The sensitivity to 9 to white light, as well as to the 3â €  
"5 increases. Spectrum image on various modifications of the bromide silver. - 55: 55 6. On  
iodized silver gelatin. â € "7. On mixed iodized silver gelatine + bromine - less breakable rays  
(curve> 5). silver gelatin.â € "8. On aggregated iodobromide silver. - 9. On Curve 5, longer di-  
semi-mixed iodized silver +. Chlorosilver gelatin. u} gestion of the emulsion just mentioned,

but it is even safer if the gelatin content of the liquid is reduced very much during digestion, e.g.  
to! /, Â

° /, of the liquid. The emulsion instructions given in the previous note can be used for this by  
taking only 2 g of gelatine during the! /, Or Â ° /, hourly digestion and adding the rest afterwards  
(immediately before solidification). Similar results are also provided by the method known as  
"Henderson's cold emulsion"?). The overall sensitive

The ability of such emulsions is very great, the reproduction of the details in the weakly lit areas

1) Photometric tests in a scale photometer (see Eder's "Detailed Handbook of Photography",  
1883, Vol. I, pag. 183) show that such bromide-silver gelatin layers are already present after h:  
give a photographic developable image for a very short exposure, however the intensity of the  
image does not increase proportionally with the light effect, but soon reaches a maximum  
which cannot be exceeded with stronger light effect. That is why such images lack the plastic in  
the brightly lit areas. |

2) Dissolve 1.g gelatin, 2 g carbonate of ammonia, 158g bromammonium, 0'2g iodine  
potassium in 50 cm? Water in the heat and then sets 5 cm? Ammonia (d = 0'91) and 140  
cmÂ® alcohol too. A solution of 20 g of silver nitrate in 100 cmÂ® of water is then gradually  
added with shaking and left to stand for 10- 12 hours (with frequent shaking) in a dark room at  
normal room temperature. Then 30 g of hard gelatine are allowed to swell for half an hour in  
water, melted, added to the emulsion and the mixture poured into 1 /, - 1 liter of alcohol, in  
which the bromide-silver gelatine is insoluble. You chop them up, wash them in running water  
for 24-48 hours, or longer in

standing water and uses it to cover plates.

About the behavior of the haloid connections etc. 9)

good, on the other hand the bright lights are blurred; it will, however, serve well in the  
photography of metal spectra. After longer attempts I was able to achieve these effect curves  
with certainty by changing the way the emulsion was presented.

Curve 3 occurs most reliably when the silver bromide is only briefly digested in a thick  
liquid (in the presence of a lot of gelatine, for example 5Â ° /, of the liquid) and some  
ammonia (rule RT)

Curve 4 results from 3 with longer digestion. Most of the commercial gelatin emulsion dry plates  
used in practical photography give similar spectrum images. Emulsions that give such curves  
are generally best suited for spectral investigations, such as the present one. Therefore, let me  
share my tried and tested method here!).



These cases clearly show that the spectral behavior of the bromide silver is related to its molecular behavior

Structure changes depending on whether it is precipitated from thick or thin liquid solutions.

#### B. iodized silver in the form of gelatin emulsion

Filled with excess potassium iodine is hundreds of times less sensitive to light than silver bromide. In the case of a very long exposure, after evoking alkaline pyrogallol, a weak image is obtained at G, which extends to Heunde oesen with longer exposure and has a maximum at G! /, F or G! /, F ( Curve 6). | |

If finished, washed silver bromide gelatine is mixed with 10% 50° /, washed iodized silver gelatine, the sensitivity of the mixture to white light decreases and the intensity of the image is mostly reduced, on the other hand the clarity increases and the plates tend less for the formation of halos. Two maxima then appear in the spectrum: One between G and H, followed by a minimum?, And another maximum (mostly stronger) between G and F, the latter being caused by the iodized silver. As a result, an emulsion made from silver iodine and silver bromine gelatine is quantitatively more sensitive in the blue than pure, matured silver bromide gelatine, the spectrum of which is represented in Curve 4 and 5. Curve 7 (FIG. 7) corresponds to the finished mixed iodized silver + bromine silver in the form of gelatin emulsion; the extension of the curve to ultraviolet and green is usually between curve 3 and 4. |

While this behavior of mixed iodosilver and bromosilver, which Abney found, was universally recognized and also clearly emerged in my experiments, as mentioned, the question remained whether these two maxima were to be found after a long digestion of such emulsion remain upright or merge, as Schumann had indicated, which was doubted by other quarters.

In my experiments, the separate maxima of bromine -t iodized silver at 7, until it was thoroughly heated, actually went over into a single one, and the same when silver nitrate became a mixture of iodine-

Potassium and potassium bromide was given so that the precipitation and subsequent digestion of iodine and

1) 30. g of silver nitrate are in 250 cm<sup>3</sup>? Dissolve water and add enough ammonia to dissolve the resulting precipitate. On the other hand, dissolve 20-22g of bromammonium, 02-038 potassium iodine and 40 g of hard Winterthur gelatine in 250 cm<sup>3</sup> of warm water. The silver solution is gradually poured into the gelatin solution while shaking, the temperature of both solutions should not exceed 30° C., digested for half an hour, poured into a shallow bowl and allowed to solidify completely. After 6-12 hours, it is crushed, washed for 10 hours in running water and then the glass plates are coated with the molten emulsion. If you put the washed emulsion in a lot of Al alcohol, this is how it is dehydrated and lasts for months in the dark. "The low iodine content makes the images clearer and prevents the spectral lines from growing together without being otherwise damaging. In the first experiments on the effect of dyes, however, it is advisable to work with pure bromine emulsion in order not to confuse the result.

2) This minimum also occurs if a little potassium iodine is added to pure silver bromide gelatine and thus plates

Poured over without digesting for long, as Schumann also found,

U.N

ee closer

10 J. M. Eder.

Bromide silver took place at the same time. The sensitivity of such an emulsion to the less breakable rays was greater than that of pure silver bromide emulsion, and the maximum of the effect was somewhat advanced towards F. Curve 8 shows the behavior of iodobromide silver. A mixture of 1 mol. Iodized silver to 8–20 mol. Bromide silver worked best. Even if the emulsions richer in iodine are more sensitive to green, the lower in iodine give stronger, prettier "images, for example as soon as the silverbromide contains 0.1%, iodized silver. |

The photographic behavior of silver iodobromide emulsions suggests that a kind of double compound of silver iodine and silver is formed, which does not seem impossible, since a mixture of chlorine and silver iodine to form the same molecules results in a noticeable lowering of the melting point shows (according to Kohlrausch!) the melting point of silver iodine is 260°, compared to silver iodine (melting point 540 °) and chlorine silver (melting point 485 °). So it indicates not only the behavior towards light, but also towards heat, to an interaction of the haloid salts of silver. down. The crystallized bromochlorosilver, which mineralogically occurs as an embolite, would also be here

to consider. C. Chlorine silver in the form of gelatin emulsion

(developed with ferro citrate developer or ferro oxalate and potassium bromide) is less sensitive to white light than silver bromide. The maximum sensitivity is further to violet, respectively ultraviolet, than to iodine and bromide silver. Fig. 6, Curve shows the spectrum image on chlorosilver gelatine in the large Steinheil's spectrograph. The maximum reads at the limit of the visible violet and the ultraviolet at X; the effect reaches up to N and F (with short exposure only up to L and @): Chlorosilver and 10% iodized silver gelatine emulsion give two separately recognizable maxima: one at 7 (belonging to the chlorosilver), the other at G', F (belonging to iodized silver), as curve 9 (Fig. 7) shows. When digesting or cooking such emulsions, the two maxima equalize each other in a similar way to that of iodobromide silver, but more difficult and not in all cases. Chlorine iodine emulsion tolerates stronger developers without blurring images than chlorine silver emulsion and the photosensitivity

closer to that of the bromide silver without reaching the latter.

Exposure to dyes as optical sensitizers | on bromosilver gelatine to increase the sensitivity to light in relation to green, yellow and red rays.

Although silver bromide exhibits an effect in spectral yellow and beyond with long exposure, it is so small that the images obtained with it are thin and blurry. Professor H. W. Vogel discovered in 1873 the fact that added dyes make the bromosilver collodion sensitive (sensitize) to green, yellow and red light rays when they absorb the same?). The behavior of bromine, chlorine and iodized silver in Collodion against such "optical sensitizers" "was followed up by him, as well as Waterhouse, Becquerel and others?) And by Ducos du Hauronâ €)

and cros?) practically recovered. || =

Ä ±) Annal. Physics. Chemie, 1882, Vol. CCLIII, pag. 642.

?) Reports of the German. chem. Gesellsch., 1873, pag. 1305 and ff .; also in the Photographische Mittheilungen, Vol. IX, S = 236% u. fi. | |

3) For a complete overview, see Eder: "Detailed Handbook of Photography", 1884, Vol. I, p. 50 and Vol. II, p. 14. \*) Photographische Correspondenz, Vol. XVI, p. 193 and 229. Also Eder's "Detailed Handbook of Photography", Gerlete;

5) Photographische Correspondenz, Vol. XVI, pag. 107. Also Eder's "Detailed Handbook of Photography", 7th issue.

About the behavior of the haloid connections etc. He]:

In the meantime, photography has undergone a complete revolution with the introduction of the silver bromide gelatin process. New presentation and development methods had to be found and the "optical sensitizers" with which one stained bromosilver gelatine, proved to have such a dubious effect at the beginning that Prof. Vogel showed the inertia of bromosilver gelatine to optical sensitizers as a characteristic this "modification" of the bromide silver looked at ), although the weak sensitizing effect

z. B. was known from aniline red. Then the Attout (called Tailfer) and Clayton companies emerged with a French patent (Brevet 152645 of December 13, 1882, and March 29, 1883 respectively), according to which eosin makes silver bromide gelatin strongly sensitive to yellow; they called these plates "isochromatic" 2) and used them to photograph colored fabrics, etc.

The favorable effect of eosin was later confirmed by Schumann, and Prof. Vogel put plates on the market which were colored with an unknown and not commercially available dye "Azalin". I picked upon this matter and examined over 140 dyes

on their sensitizing effect, both theoretically and practically. About the way of coloring bromide gelatin.

This can be done in two ways: either by adding dye to the liquid

Emulsion or bathing of the finished dry plate in the aqueous or alcoholic solution. Quantity of dye added.

The correct concentration of the dye is the first requirement for success, which I assume to be known. Too much depresses the general sensitivity, in that too thick layers of dye over the bromide-silver inhibit the admission of light too much; often the maximum effects are then blurred. Too little dye allows the effect of the optical sensitizer to subordinate too much to the intrinsic sensitivity of the bromide silver.

The best concentration is different for different dyes. It is best to try an addition of 2-4 mg per 100 cm<sup>2</sup> Emulsion or the same amount dissolved in water, which solution is then used as a bath for the dried plates (in 2 to 5 minutes). Dyes with a strong tinging power must be used more diluted, others ten times more concentrated. Eosin, for example, is enough! / ., mg per 100 cm<sup>2</sup> To sensitize the emulsion noticeably in yellow-green with the characteristic stripe, although the eye does not perceive a reddish color. The dye can appear to wash out completely from such gelatin emulsions for many hours

and yet its sensitizing effect can be clearly demonstrated in the spectrograph. Effect of various dyes on silver bromide gelatin.

Of the large number of dyes investigated, only a part proved to be optical sensitizers for silver bromide gelatin. When it comes to the effect of these, one must distinguish:

1. The influence on the overall sensitivity of the colored silver bromide gelatin plate. Often the light sensitivity for the blue and violet part of the spectrum is reduced so that it only possesses, for example, the original (most

the purple and green ones I examined and many other dyes show this property).

1!) Photographic News, 1883, p. 426. 2) Photographische Correspondenz, 1884,

p. 63. 9 \* ee eEErEESEETEEEEIEICITTLÜLTEITEELEEE

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2. The influence on the relative sensitivity for yellow, orange, etc. Regardless of whether the sensitivity of the colored bromosilver gelatin for the blue part of the spectrum decreases or not, it often increases as a result of the effect of the dye for yellow, orange etc. For example, in the case of silver-bromide gelatine plates, the addition of rose bengal reduces the sensitivity for blue to 1/3, or 1/4, while the sensitivity for yellow-green (near line D) is much greater than for approx Torn plates (compare also with cyanine). Here the overall sensitivity decreases and the relative yellow-green sensitivity increases, so that such colored plates have to be exposed for example 3 to 6 times longer to give a photographic image in daylight. blue ones, on the other hand, are just as strong as uncolored ones.

If a photographic plate is to reproduce the colors with the same brightness effect as it appears to the human eye, then the orange (for C) and light blue (for F) should appear approximately the same in the spectrum, yellow (for D) 8 times and yellow-green (for D) about 10 times, green (at E) about small stronger than light blue, but violet only have a tenth part of the effect of the latter. Up to now, no method has been described which meets these requirements; but it is possible to weaken the blue by switching on yellow glasses to such an extent that the yellow-green appears much stronger than blue and violet on the colored bromide-silver plates, as for example Curve 17 (Eosin plates exposed through yellow glass) shows. However, the effect in red or orange is still missing here. For those plates, which by optical or chemical means all colors with the same brightness effect (brightness value), which these for have the eye, reproduce photographically, I suggest the name "orthochromatic plates". It is well known that the photographic plates in use now give the orange and yellow much darker (almost black) than the dark blue and violet, which appear almost like white.

Hofmann's violet, as well as various commercial varieties of this color, such as dahlia, primula, iodine violet (E), cause the bromosilver gelatine to be more sensitive to orange, yellow and green, both in water and in alcohol-soluble varieties. The overall sensitivity decreases, the increased orange sensitivity has the maximum between D and C (somewhat closer to D). With a short exposure, this maximum occurs in the position of curve 10; with longer exposure, the effect extends over C against Roth and can be followed through the green - with a minimum between D and E -. The methyl violet, violet de Paris

and especially the benzylrosaniline violet (methyl violet 6 B), gentian violet B, gentian violet DR, and acid violet also have a very similar effect. The increase in sensitivity in orange occurs in pretty much the same place for all of these dyes; only now and then the maximum emerges steeply and strongly (curve 10), in other cases (with changed concentration and longer exposure) the curve of the effect gradually extends to a weak maximum between D and C increasing, very flat in orange to towards red in B. The intensity of the effect in blue on such colored bromide-silver gelatine is greater than in orange. |

Of the green dyes, acid green, bitter almond oil green (in the commercial grades solid green, malachite green, ne green, benzal green), furthermore ethyl green (solid green J, brilliant green) and methyl green show the maximum red sensitivity for  $\hat{A} \odot$ . In the case of a short exposure, the effect of the hardly breakable rays is limited to this more or less clearly expressed maximum (curve 12); with longer exposure, however, an effect is noticeable up to B in the red, as well as in a weak degree over yellow and green; on the other hand

creates a much stronger image in blue to ultraviolet. These raise awareness of the said greens

!) The yellow and red sensitivity of common uncolored bromide silver gelatine is so low that you cannot photograph a painting with the correct brightness value of the pigments despite the yellow glasses being pushed in front. ?) Used as a bath in 30-40% alcohol; likewise the other "alcohol-soluble" violets.

About the behavior of the haloid connections etc. 18

Dyes for red can only be detected in strong direct sunlight and correctly chosen concentration; so it cannot always be recognized with certainty. The same applies to aldehyde green and chlorophyll!), Which in my experiments very rarely caused the bromide-silver gelatine to be significantly red-sensitive.

Iodine green showed the maximum effect in one variety between D and  $\hat{A}, \neg$  in orange (curve 15) and was sensitive to red up to almost  $\hat{A} \in ^{\text{TM}}$ ; in other varieties (which appeared less blue-green) the maximum was further towards C in the red. Apart from the reduced overall sensitivity of the plates stained with iodine green, they showed the best sensitivity of all to the external red. The experiments succeed with significant dilution as well as with greater concentration.

Cyanine is a very good sensitizer for orange and red with bromide gelatine, as I discovered at the same time as Schumann. This applies primarily to iodocyanine, which is the common cyanine (quinolinjodeyanine?). In addition to the strong blue effect, a short exposure also results in a less strong effect between D  $\hat{A} \frac{1}{4}$ ndee XD, C to DI, C), while in green and yellow only a little blackening is noticeable (Curve 14). With longer exposure the effect extends continuously from the blue part to B im Roth. A minimum of the effect occurs before E (F? /, E); then a weak one follows

not always easily recognizable maxi

mum before D ( $\hat{E} \hat{A} \text{ } ^{\circ} ? /, D$ ) and that

mentioned stronger at D! /, C. The

predominant

| 10 and 11. Spectrum image on silver bromide gelatine dyed with methyl violet, but the main effect occurs if one uses Violet de Paris, Benzylrosaniline Violet, Iodine Violet, Dahlia, Gentian Violet, Acid Violet. â€"12. The same with acid green, solid green, methyl green, brilliant green. â€"13. With iodine green. â€"14. With cyanine. â€"15. With bromine-eosin. - (Curve 14). The situation is very similar. 16. With rose bengal + ammonia.

no yellow glass advances, in the blue

Chlorine-cyanine, sulphate-cyanine and nitrate-cyanine, however the iodine-cyanine has the most favorable effect on the sensitivity of the plates stained with it; in all four types of cyanine the maximum orange sensitivity is in the same place. The overall sensitivity of the cyanine pla The killing against white light is less than that of uncolored plates (maybe! / , , or! / ,), but the relative orange sensitivity is more than 100 times greater. When working with it, you always have to use subdued dark red light and work in the shade if possible. Schumann recommends dimming the red light with brown paper, which I also found practical.

If a little ammonia is mixed with the cyanine with which the emulsion is colored), the maxima of the effect emerge more strongly.

1) Chlorophyll sensitizes bromosilver collodion well to red and orange (Becquerel, Ives et al .; see Eder's "Detailed Handbook of Photography", 7th volume).

2) New handbook of chemistry, Vol. II, pag. 583.

3) A bath of 100 cm<sup>3</sup> of water is also good, 2 cm<sup>3</sup> alcoholic cyanine solution (1: 400) and a little ammonia.

14 KEN »Redser:

Eosin and the eosin dyes derived from it are all very good sensitizers "for green, yellow-green and possibly for yellow. With these dyes, the effect of the optical sensitizers is not difficult to study and to prove even in scattered daylight.

I tried bromine-eosin in the commercial varieties: eosin yellowish or eosin J, pyrosin J, erythrosin yellowish. With short exposure, in addition to the usual silver bromide spectrum, all gave a maximum of the dye effect between E and D (E ' / , D), while no effect was noticeable between E and F (curve 15).

With longer exposure, the maximum increases in the yellow-green, the effect extends steeply down to D; on the other hand, the curve also falls towards E and reaches a minimum between F and & (E ' / , F) (curve 15). Addition of ammonia in the amounts given above increases the effect in the yellow-green; the maximum occurs more intensely and the effect is also somewhat more visible to the right and left of the maximum. At the same time, a second weak maximum of the dye effect at E - which is otherwise hardly noticeable - appears a little more clearly; it is indicated in curve 15.

The bluish nuances of eosin colors have an absorption band further in the yellow. Accordingly, the band of optical sensitization is also closer to line D. This applies to the bluish tinge of eosin (eosin B) and the bluest of all eosins: rose bengal!), The effect of which I first announced in April 1884 in a provisional

communication ?) made known. The spectrum with rose bengal containing silver bromide gelatin shows Curve 16 with short and long exposure.

In the presence of ammonia, the maximum at D is much more pronounced; the effect then - provided there is ample exposure - extends further against the less refractive rays. Between the main effect in blue and the weaker maximum at D there is a less clear one at E, which mediates the transition between the effect in yellow and blue.

" The other eosin colors also turned out to be optical sensitizers for yellow-green and yellow, namely: methyl eosin (methyl erythrin), ethyl eosin, phloxin (potassium salt of tetrabromodichlorofluorescein), cyanosin (methyl ether of phloxin), aureosin (chlorofluorescein) and safrosine (bromonitrofluorescein). The band of sensitization lies between that of eosin and rose bengal, depending on the position of the absorption strip. However, the achievable sensitivity to light is not the same for all of them, but rather, for example, lower with cyanosin and phloxin than with eosin.

If the sunlight is allowed to fall through yellow glass or a solution of potassium dichromate (1:1000) before it enters the slit of the spectral apparatus, the ultraviolet, most of the violet, and the blue are considerably weakened. This increases the relative brightness of the spectrum in the yellow-green, yellow and orange. Silver bromide gelatin correctly colored by eosin then gives a spectrum image in which the blackening in yellow-green, that in blue, etc., by far predominates. Curve 17 shows this effect. Plates which reproduce the colors in this way are good to use for the photography of yellow and blue colors, because yellow also appears to the human eye about the same amount lighter than blue and violet.

The red sensitivity of the eosin colors is, however, insufficient and the green sensitivity relatively too great.

Curve 18 shows the spectrum image on a silver bromide gelatin plate which is colored with a mixture of eosin and cyanin. The dotted curve 18 corresponds to an excess of eosin, the solid curve to an excess of cyanine.

However, these dye mixtures do not show the pure effect of each in the spectrograph. One interferes with the other. Emulsion colored with cyanin + eosin

Ä ±) Sodium salt of tetraiodochlorofluorescein. ?) Photographische Correspondenz, 1884, p. 95; also p. 2 of these treatises.

About the behavior of the haloid connections etc.

165)"

has a lower red sensitivity

delicacy than that colored with cyanine alone; in the mixture of the

two the sensitivity to yellow-green has also decreased. Nevertheless,

by mixing.

Colors reduce the relative sensitivity for the less breakable rays to a larger number

Different colors of the spectrum can be expanded by taking the minimum of the effect of the one

Makes the dye disappear by adding another dye, which is there at its maximum

Has. My experiments justify the hope that in this way a uniform sensitivity of the bromide silver can be achieved for the entire spectrum without individual maxima and minima emerging.

Aniline red sensitizes to yellow and greenish yellow. I tried rosaniline hydrochloric acid and acetic acid, as well as Coupler's toluene red!) With equal success. The maximum of optical sensitization is  $\lambda \approx 400 \text{ nm}$ , D; the effect extends weakly to over D and, on the other hand, runs with a minimum at E to blue, violet and ultra-violet (Curve 19, see 9). With a short exposure - before the effect appears in the yellow - the effect in the violet and ultraviolet is weakened on the plates dyed with aniline red and a strong sensitivity to blue emerges between G and F (dotted curve 19). It strikes me that acid foxin (rosaniline sulfosate sodium) in my preparations did not cause the same sensitization in yellow as aniline red, but also a weakening in violet.

With fluorescein and ammonia I got dry bromide

silvergelatin plates raise awareness

N E T N N

Fig. 9.

=>

17. Spectrum image on silver bromide gelatin colored with eosin (through yellow Glass). - 18. Same with cyanin + eosin. - 19. Aniline red.  $\lambda \approx 400 \text{ nm}$ .

Fluorine

escein + ammonia (solid curve: wet; dotted curve: dry). -

21. Resorcinol blue.  $\lambda \approx 400 \text{ nm}$  22. Rothes Corallin.  $\lambda \approx 400 \text{ nm}$  23. Naphthalene red. - 24. Bleu-Coupler.  $\lambda \approx 400 \text{ nm}$  25. Safranin.  $\lambda \approx 400 \text{ nm}$  26. Chrysaniline.

Green up to the vicinity of D, without observing a maximum protruding there (dotted

Curve 20), on the other hand wet (after long exposure) a maximum of the effect occurs in the green, namely

a band with a recognizable maximum near E (solid curve 20); as a result of the long

Exposure makes the image appear very intense. An effect similar to that of dry fluorescein shows

Chrysoline (benzylfluorescein) on silver bromide gelatine, only the effect is more intense and extended in the green

further into yellow (up to over D). Both dyes do little damage to the overall sensitivity.



1) D. i. Aniline red from aniline and nitrotoluene, see "New Handbook of Chemistry", Vol. I, p. 620; also

M. Vogel: "The Development of the Aniline Industry", 1870, p. 177,

oe J. M. Eder.

Even with resorcinol blue (Bleu fluorescent ') I only got a (albeit slight) sensitization on wet plates soaked with the dye solution, which extended up to C (curve 21). With short exposure (similar to aniline red) the effect in the blue is particularly pronounced because the effect of the ultraviolet and violet is reduced. |

Corallin didn't always give me certain results, except for the "Red Corallin" variety. Both by itself and in the presence of ammonia, this produced a moderate increase in the sensitivity in the yellow of D. The effect extended into the orange towards C and gradually increased to an intense effect, as a minimum appeared in E! /, D in blue above (Curve 22, Fig. 9). Acids reduce the effect. ||

Naphthalene red (Magdalaroth) gives a strong maximum of the yellow effect in D. With short exposure, this maximum is separate, then the blue-green effect begins again, which extends into the ultraviolet (dotted curve 23). With longer exposure the effect reaches into orange and runs with weak green sensitivity towards the breakable end of the spectrum (Curve 23).

Bleu-Coupler (sulphonic acid of violaniline obtained by the nitrobenzene process) causes a sensitization for the less breakable rays, which is remarkable because (in addition to the usual maximum for silver bromide gelatine in blue) two maxima apply: one in green (E \* /, D), the other in orange (D \, C), as Curve 24 represents. It seems possible that the Bleu Coupler before me is not a pure dye, but a mixture of two different dyes. |

Safranin is a good sensitizer for green. If the exposure is long enough, its effect extends to slightly above

D. The effect in green did not increase to a strong maximum in my experiments, but rather extends up to E, after which the curve of the effect against blue rises rapidly (curve 25). Certain types of Ponceau also have a similar effect, e.g. B. Ponceau 3 R, Piiienelpomeeau,. "Bibericher.Scharlac hr (the

Aeic2 probably only to a slight extent). some grenadine (a waste product in the production of aniline red), which shortens the spectrum image at both ends and makes it stronger with short exposure, but sensitizes up to D with longer exposure.

Chrysaniline is a good sensitizer for green. Dr. Lohse?). I found this dye also effective in neutral aqueous solution. He altered the effect of the solar spectrum on the bromide-silver gelatin dyed with it in a strange way.

The effect of the violet and ultraviolet decreases, in the blue (at G @? /, F) there is an intense blackening, which gradually decreases towards Es =, runs through the green and disappears before D (Curve 26, Fig. 9). As a result, the curve appears shifted further towards green compared with that of the uncolored silver bromide gelatine. The blackening due to the sensitization of chrysaniline in green is so closely related to the normal spectrum on bromide silver that no interruption can be noticed, which is also the case with chrysoline, by the way.

Many dyes do not give a clear sensitization maximum in green, yellow or red on silver bromide gelatine, but influence the spectrum image on silver bromide in the blue and violet parts.

For example, acid fuchsin, dry resorcinol blue, aniline red (with short exposure),

) Benedict: "The artificial dyes", 1883, p. 171.

2) cf. "New Handbook of Chemistry", Vol. IV, under "Naphthalene" and "Naphthalene dyes".

3) Dr. Lohse found a concentration of 0.004 g of dye, 2 cm<sup>2</sup> Ammonia and 100 cm<sup>3</sup> Water as sensitizers for yellow-green and green: chrysaniline, nitric acid chrysaniline, hydrochloric acid diamidoazobenzene. On the other hand, the following yellow dyes are not or not very effective: orthonitrophenol, orthonitroaniline, paranitroaniline, metanitroaniline, thymoquinone, phenanthroquinone, chrysophanic acid, tropaeolin 00, quercitrin, yellowwood extract, aloe, diamidobenzene, amidoazobenzene, diamidobenzene, picolinobenzene, nitrosodimethylgel Tropaeolin J (Photographisches Archiv, 1884, pag. 221; also Photographische Mitteilungen, Vol. | XXT, pag. 130).

About the behavior of the haloid connections etc. 17

Corallin (with short exposure) and many others, both yellow, red, violet and blue dyes weaken the ultraviolet and violet, whereby the blue appears relatively stronger and the general sensitivity decreases (Curve 27, Fig. 10). In this way it seems possible to suppress certain parts of the spectrum.

Other dyes sensitize silver bromide gelatine to the less refractive rays without a clear maximum. In the case of silver-bromide gelatine plates, which are coated with weakly ammoniacal hematoxylin, ammoniacal curcumin, soluble Berlin blue, hydrochloric acid monophenylosaniline and others. are colored, the effect of the solar spectrum can be traced into yellow and further into red (curve 28). However, I never got that clarity in the photograph of the Fraunhofer lines, as when using dyes with a strong maximum of the sensi-

bilization, but mostly is the

picture Fig. 10. N M L K H 6 F E

D C B A

hazy and hazy as if it were

would have been exposed for too

long. Iodobromide silver gelatin and

colorants.

Mixtures of finished silver iodine gelatine and silver bromide gelatine give, as mentioned above, a spectrum image which consists of two (by a minimum

shows separate) maxima; namely that

one in purple. the other in blue. If such layers are stained with eosin 27. Spectrum image on bromosilvergelatine, stained with acid fuchsin, resorcin

their arbutofe so come blue etc. with short exposure.  $\lambda \in \text{''}28$ . The same with hematoxylin, soluble Berlin blue etc.  $\lambda \in \text{''}29$ . Iodized silver + bromide silver, colored with eosin. a third maximum in yellow-green  $\lambda \in \text{''}30$ . Chlorosilver gelatine with eosin.

or at the point characteristic of the optical sensitization. Curve 29 (Fig. 10) shows the spectrum image on iodized silver + bromide silver, colored with eosin. The maximum of the eosin action lies between E and D, precisely at the point where it is found in pure silver bromide gelatine, and indeed only a single band, which is nowhere interrupted by a minimum, is present at the point of optical sensitization; In addition, there appears the characteristic spectrum image on iodized silver + bromide silver in the blue part, so that in all there are three maxima. The other dyes behave in a similar way. Iodobromosilver gelatine, in which the two maxima have merged through digestion (see pag. 8, curve 7 and 8, Fig. 7), has the maximum of the optical sensitization caused by dyes also at the same point as bromosilver gelatine.

With a content of the bromide silver of  $1 \lambda \in \text{''}3\text{\AA}^\circ /$ , iodized silver becomes the effect of the coloring agent

is not noticeably modified. "But if the iodized silver content rises to 10-30", then the dyes, as far as I examined them, no longer sensitize that much. strong for the less breakable rays. Schumann observed that pure iodized silver gelatine!) Cannot be sensitized at all to yellow-green by eosin, which is so easy with bromide silver; this behavior of iodized silver explains the phenomenon mentioned above.

Chlorosilver gelatin is acted upon by eosin, cyanine and others when silver

bromide Strongly sensitized dyes. In this case too, the dye effect is at its maximum

1) The iodized silver was precipitated with excess potassium iodine and the finished emulsion was created with alkaline pyrogallol. B)

18 | J. M. Eder.

same place as for silver bromide gelatine. In addition, the spectrum comes into play in the violet part in the manner characteristic of chlorosilver. Curve 30 (Fig. 10) shows chlorosilver gelatin colored with eosin. On short exposure (dotted curve 30) a maximum appears at  $77^\circ$  at the beginning of the ultraviolet; in the blue and green no effect is noticeable, in contrast to E  $^\circ$ , D the eosin effect is more pronounced. With longer exposure, a faint effect runs through blue and green to yellow, where sometimes a maximum appears which exceeds that in violet.

| Mixtures of iodized silver with chlorosilver gelatine, as well as bromide silver with chlorine silver gelatine, behave towards dyes in the same way as iodized silver mixed with bromide silver. Chlorine silver with  $10 \lambda \in \text{''}20\text{\AA}^\circ /$ , iodized silver gives clear and strong images after the addition of eosin with very strong relative sensitivity in the yellow-green, which usually exceeds the colored bromide silver.

Influence of uncolored substances on the color sensitivity of the bromide silver gelatine.

If you bathe common silver bromide gelatine plates in a very weak, preferably slightly acidified, alcoholic silver nitrate solution!) And dry them, their sensitivity to white light increases two to three times. In the solar spectrum, this effect first emerges as an increase in "the overall sensitivity, but on closer inspection one finds that the relative sensitivity to the less refractive rays has also increased somewhat. Ammoniacal silver solutions have the same effect, but they make the image stronger Such plates,

however, only have a shelf life of one day and in terms of color sensitivity do not come close to the colored plates.

If an eosin-colored silver bromide gelatine plate is bathed in a weak (preferably alcoholic) silver nitrate solution, eosin silver is formed?) Next to excess silver nitrate; such plates are then generally more sensitive to white light and relatively more sensitive to yellow-green®). Other dyes behave in a similar way.

If you bathe DBrom silver gelatine plates in dilute ammonia for a few minutes and dry them, they appear about twice as sensitive to white light and give much more intense images.

Such plates generally prove to be more sensitive to the solar spectrum in the same ratio, without an increase in sensitivity to less refractive rays becoming particularly apparent. The blackening, however, becomes much more intense in the entire spectrum image. If sensitizing dyes are added to the diluted ammonia, the sensitizing band also appears stronger.

The effect of the ammonia, which completely evaporates again during drying, can only be traced back to a molecular change in the bromide silver, which has a great influence on the photosensitivity of the same, as I have already shown in my earlier treatise.

The solution of silver bromide in ammonia does in fact leave behind microscopic crystals when it evaporates, as Elsdon®) has shown; even with the precipitation of bromide silver in the presence of a great deal

1) 100 cm? Alcohol and 0: 1-0'5 cm? a 10% aqueous silver nitrate solution.

2) Using common developers.

#) Eosin silver on its own is sensitive to yellow according to H. W. Vogel (with D towards green); this behavior was first made known by Robert Amory in January 1878 in the American Academy (Journ. Photograph. Society Great Britain., June 1884). |

\*) The images can be clearly developed in pyrogallol as iron oxalate and copy well.

5) 1-10cm? Ammonia and 100 cm? Water.

6) Photographic News, 1881, p. 174.

About the behavior of the haloid connections etc. 19

They form ammonia. Depending on the concentration of the solution, they have the shape of Fig. 11a ') or Fig. 1152), a size of 0:02-0'2 mm and a thickness of approximately 0'001 mm. Crystals of this size are formed when bathing silver bromide

gelatin in dilute ammonia does not; alone Ba:

when the ammonia evaporates from the moist

Plate is the bromide silver oh ne doubt crystal- 5 ne a> Å © N = linear and this likes the increased quantitative

Cause photosensitivity.

Caustic potash and alkali carbonates also increase  $\hat{A}^\circ$  || Be = En ae Se

\_ Sensitivity, taking it as bromine absor- Crystallization of silver bromide with ammonia in the microscope. Drinking agents should work. Large quantities

however, these additives have not found use in the practice of making silver-bromide gelatine plates because the durability of the latter would suffer as a result. On the other hand, adding very small amounts of bromammonium and soda to the emulsion before pouring proved to be sensitive

beneficial. Sodium sulfite also acts as a moderate sensitizer.

Experiments on the chemical nature of the bromide silver, which is mixed with colorants and gelatine.

For the assessment of the phenomena which bromide silver shows in a colored or non-colored state in the solar spectrum, as well as the role which gelatine plays in this, the decision of the question is of importance: Does bromine silver combine with the substances mentioned or Not? The same test conditions must be observed here as for the preparation of a light-sensitive silver bromide emulsion. If silver bromide gelatine emulsion is prepared in the usual process, washed and then spun out in a liquid state in a centrifugal machine, the silver bromide can be separated from the gelatine. Mr. J. Plener has constructed a machine for cleaning the bromide silver to be used photographically, which he kindly put at my disposal for these experiments. Fig. 12 shows the cannon bronze vessel used, which is well gilded on the inside. At a, the container filled with the liquid emulsion and then closed at c is attached to a vertical axis, which is then rotated at a speed of 4000-6000 revolutions per minute. Due to the centrifugal force, all the silver bromide is attached to the walls of the

barrel at bb and there forms a coherent mass,

so that the gelatin solution can be clearly poured off and the silver bromide can be washed with water. In this way you can use the silver bromide centrifugal apparatus for

\* {l. ; spin completely clean and wash from bromide silver?). Bromide silver, which by means of the Emulsions. Centrifugal machine by repeated spinning and washing with

hot water was freed from all soluble substances, according to my analysis, after drying at  $140\hat{A}^\circ \text{ C.}$  - whereby a lot of hygroscopic water escaped - still contained organic substances, which by glowing and converting the resulting silver into bromide silver (with Bromine) quantitative

were determined.

1) When the concentrated ammoniacal silver bromide solution evaporates after diluting it with five times the amount of water.

2) Like the previous one, after diluting with the same amount of water.

) It. disperses instantly in a fresh gelatin solution to form a fine emulsion with excellent photographic properties.

20 - JNrechrdest.

100 parts by weight of silver bromide contained in one case 0 ° 45 parts, in another case 0:52 parts gelatin.

This shows that during its precipitation the silver bromide absorbs the latter in the presence of gelatine and holds it so stubbornly that it cannot be removed by washing with hot water and centrifuging.

If eosin or cyanine is added to a gelatin emulsion and the same is then washed, the dye can no longer be removed so completely that the sensitivity to yellow would not become apparent in the spectrograph. But when the silver bromide was centrifuged out of eosin-containing silver bromide gelatine and washed, and the centrifugation and washing were also repeated three times, gelatine initially colored red came off, but later the washing water was colorless. Nevertheless, the silver bromide remained slightly reddish when larger amounts of dye were used, or appeared barely discernible when less eosin was used. In all cases, however, the maximum sensitization characteristic of eosin occurred in the vicinity of D. .

This proves that the colorant adheres firmly to the grain of silver bromide itself, be it the silver bromide as such or the gelatine enclosed by the grain of silver bromide).

This fact appears to be relevant for the attempts to explain "optical sensitization".

Relationship between the absorption of the dyes and their sensitizing effect for silver bromide.

For the assessment of the connection between the absorption of the dyes and their sensitizing effect, to which HW Vogel has already referred in general outlines, I chose colored, dry gelatine foils?) And compared the absorption with the spectrum photographs on the as well colored bromide silver gelatin plates. In all of the cases I have observed the position of the absorption spectrum of the dry, dyed film corresponded to the sensitization maximum on dyed bromosilver, although there was a shift in the latter towards Roth compared with the former. However, this shift is not always very significant; in the case of eosin dyes, the maximum | differs the absorption of the gelatin film and that of the sensitization to silver bromide in the yellow-green around 16-20  $\mu$ ).

In Fig. 13 the results of some of my experiments are shown. Spectrum 1 is the facsimile of the spectrum image on bromosilver gelatine, which was colored with bluish eosin, preserved in direct sunlight (similar spectrum images on yellowish eosin and rose bengal are shown as curves on p. 13). Figure 2 shows the absorption spectrum of a dry gelatine film colored with the same eosin (using a photographic image of the same on cyanine-bromide-silver plates). The maximum of the sensitizing effect of eosin on bromosilver gelatine is further towards Roth than the maximum of the absorption in the colored gelatine. The same is true of aniline red, as shown in Figs. 3 and 4 in Fig. 13, and of the other dyes.

Thus, through the colored gelatine, many rays still pass through at the less breakable end of the spectrum, which have an extremely strong effect on equally colored bromide silver. One lets

!) The gelatine would then mediate the adhesion of the dye to the bromide silver in a similar way as all protein bodies do when dyeing cotton.

?) Dye solutions give completely different absorption spectra than dry dyes. Colored bromide silver plates would have worked best; however, since these are difficult to make, I content myself with colored gelatine foils.

“) Following Kayser's suggestion (“Textbook of Spectral Analysis”, 1883, pag. 11), I denote the wavelengths in millionths of a millimeter =  $\mu$ .

About the behavior of the haloid connections etc. >

If the solar spectrum falls through a dry gelatine sheet dyed with eosin, no photographic image in yellow-green should appear on eosin-bromide-silver gelatine if the rays absorbed in the former would excite the photosensitivity of the latter, as was assumed from another side. But under these circumstances I received, in addition to the usual spectrum image in blue, also an intense image in yellow at D, which corresponds to the maximum of the optical sensitization on eosin-bromide silver and next to it a minimum (a completely empty space), which corresponds to the maximum absorption of the eosin gelatin (curve 5 in FIG. 19).

This proves that the maximum of sensitization in colored silver bromide gelatine plates is not identical to the maximum absorption in colored gelatine, but that the coloring of the silver bromine itself must be taken into account. I have shown experimentally that the bromide-silver molecule is actually colored (p. 19); To explain the larger shift in the maximum of the photographic sensitization of bromosilene associated with light absorption, the Kundesche Geserz can be cited, according to which in!

most cases with the increase

due to the refractive power of the medium, the absorption strips of the dye it encloses are shifted towards the red end. On

1 a

INN IUER!  $n_l$  |

Dr. E. Albert?)

for colored: Collodion emulsions on ii

made noticeable.

Believe through this  
observation a

| I also see the behavior of silver bromide

1 |gelatine, which is under a coloring

1. Spectrum image on silver bromide gelatine + eosin. 2. Absorption spectrum solution is exposed while it is still wet, a gelatin sheet stained with eosin. 3. Spectrum image on bromide silver Maren: to. can? The dye solution gelatine + aniline red. 4. Absorption spectrum of an aniline red

colored gelatin foil. 5. Absorption spectrum of one stained with eosin

then acts like a colored umbrella. For gelatine foil, photographed on an eosin-colored silver bromidegelatine. Example resembles the spectrum image on one

silver-bromide gelatin plate covered with aqueous eosin solution more to picture 5 in FIG. 13 than to picture 1 in the same figure; the absorption strip of the aqueous eosin solution lying at E blocks the light from the silver bromide underneath and limits the effect to the maximum of sensitization that lies further towards D, the latter for dry or wet colored silver bromide is almost in the same place. If you color silver-bromide gelatine with mixtures of dyes, the effects of the same are often damaged, and it is not uncommon for one to appear to be suppressed. This case seems to occur especially when the absorbent strip is colored with a component

Gelatin over the sen sensitization maximum of the other component falls.

Relationship between the abnormal dispersion of the dyes and their sensitizing effects to silver bromide.

Most of the dyes that have a sensitizing effect on silver bromide

abnormal dispersion detected and Dr. E. Albert suggested that the abnormal

1!) Photographic Correspondenz, 1884, p.

137.BE,

29 PEMe @ Brdter

Dispersion in connection with sensitization is: «Silver bromide is mainly affected by small-wave (blue and violet) dyes. Due to the abnormal dispersion, rays of small wavelengths are now brought to the red end of the spectrum (next to the absorption strip), which have a strong effect on bromide silver. This, says Albert, would explain the shift in the maximum of the chemical action towards the red end of the spectrum in a casual way; however, he only expressed the presumption without further experimental investigation. |

I use F ig in my arguments. 14 from Schellen's Spectral Analysis (1883).

In the normal spectrum (1), rays of ever smaller wavelengths follow one after the other from left to right. In the abnormal spectrum of a concentrated aniline red solution acting as a prism, the absorption stripe is £ and on both sides the halves of the normal spectrum appear shifted from one another. On the right are the rays of greater wavelength (red, orange, yellow and yellow-green), to the left of the absorption strip, however, the rays of shorter wavelength (violet to blue-green). Thus in the abnormal



spectrum of the fuchsin the rays of light C to D! /, E have exactly the same wavelength as in the normal spectrum the rays G to H7, which act most strongly on silver salts. \_ |

It is now difficult to see how a dye should produce abnormal dispersion in a normally generated pure solar spectrum, and on closer inspection one encounters other contradictions. At first it seems striking that dyes give a narrow, intense band of sensitization in yellow, etc., while in the normal blue and violet part of the solar spectrum they often form an elongated stripe without a clearly limited maximum.

mum show. In a nutshell, the sensi-

biliÄ ± sation effect in yellow or red a similar one

1. Normal solar spectrum. - 2. Bring out abnormal spectrum of K rotate image, as in the blue part. It should

namely in iodine-bromide-silver gelatine or iodine-chloro-silver gelatine, which show two maxima in action in the blue end of the normal spectrum, two maxima in the sensitization band are also noticeable in the yellow end due to the abnormal spectrum, which I never observed when the dye was only one Had absorption band.

Furthermore, if the dye produced a band of small-wave rays at a certain point in the spectrum, the maximum of the sensitization by a dye would have to be different for bromosilver and chlorosilver gelatins, because chlorosilver has the greatest decomposition in H and silver bromide @ to F suffers. As a result, the maximum sensitization for silver chlorine should be much less against Roth than for silver bromide. However, attempts with eosin and cyanin gave me negative results. The maximum of the normal spectral action of colored chlorine, bromine, iodine bromine and iodochlorosilver gelatins in the blue part of the spectrum fluctuates according to the nature of the silver salt (p. 17), but the position of the maximum of sensitization by dyes in the red end is constant ).

The abnormal dispersion is not enough to explain the sensitizing effect of stains! Bromide silver etc.

According to other researchers, their sensitizing effect on silver bromide is not related to the fluorescence of the dyes and I can do this on the basis of my experiments

confirm. There are dyes that fluoresce red (naphthalene red), as well as sensitizers,

!) I disregard small irregular fluctuations, which I attribute to the influence of the atmosphere on the quality of the light.

About the behavior of the haloid connections etc. 23

such as those that fluoresce yellow (certain eosin colors) or green (fluorescein); on the other hand, some non-fluorescent dyes (cyanine, aniline red) have a sensitizing effect; briefly there is no rule

moderation in that direction.

Relationships between the chemical and physical properties of substances and their sensitivity to light.

Not all dyes bring about a relative increase in the photosensitivity of the silver halide salts to the lessrefractive rays to the same extent, and many not at all.

I have over 140 dyes on silver bromide gelatine in two to three different concentrations, as well as atleast three of different lengths (around 100-8300 times BC)

variable) exposure times and was only able to find sensitizing properties in the case of a fraction. Even if the number of sensitisers discovered by me is a considerable one, they are only to a lesser extent intensive.

Within very narrow limits, with a similar chemical constitution, homologous absorption spectra and sensitizing effects occur, for. Example with iodine, chlorine, sulfate and nitrate cyanine, with various salts of rosaniline etc. Yes, I will. this doesn't say much. The fluorescein derivatives seem to have the said property more generally, for example fluorescein and benzylfluorescein (chrysoline) are sensitizers for green, the brominated, chlorinated and iodinated fluoresceins (eosins) for yellow-green to yellow, on the other hand this regularity is negligibly small Effect of the nitro derivative disturbed.

Since fluorescein is a phthalic acid derivative, namely resorcinophthalein, I tried phenolphthalein (with red alkalis) and orcinophthalein (red) as well as the bromination and nitration products of the latter, butwithout notable success.

Rosaniline salts sensitize people to yellow and orange; Rosaniline sulphonic acid (red) not, whereas the sulphonic acids of bitter almond oil green (i.e. acid green) and bitter almond oil green themselves sensitize. Trimethylrosaniline, as well as triaethylrosaniline salts (Hofmann's violet etc.) sensitize for orange to red, phenylrosaniline and their sulfonic acid salts (aniline blue) but not remarkably.

I could not find any regular relationships between chemical constitution and the sensitizing effect of the dyes.

This succeeded better with the position of the maximum absorption of the colored light of the dye and that of its sensitizing effect on silver bromide gelatin. From the former one can infer the latter and it will be possible to determine in advance whether the dye sensitizes the bromide silver in green, yellow or red. One will consider the absorption spectrum of colored gelatine foils and take into account the above-mentioned shift of the sensitization strip according to Roth. This applies to Miesaller Rarbstotlfe, which are sensitizers [for-bromosilver selatins].

The question now arises: Which dyes are sensitizers? I know of no other sure means than to find out more about it through the photographic experiment. According to the observations I have received so far, the dyes that have a sensitizing effect on silver halide salts must meet the following requirements:

1. You need to color the silver bromide grain. The dyes that strongly sensitize are also all so-called "substantive dyes".
2. In the dry state - on colored gelatine or, more correctly, on colored bromide silver - they must show an intense band in the absorption spectrum, even in considerable dilution, if they are to bring about anintensive blackening of the bromide silver. A narrow band of absorption

there is also such a thing when it comes to raising

awareness.4 J. M. Eder.

I mentioned above that neither fluorescence phenomena nor abnormal dispersion of the dyes adequately explain their sensitizing effect on silver bromide for the less refractive rays.

The assumption that instead of the absorption strip the molecules of the dye are set into energetic oscillation and thus also the neighboring bromide silver is untenable, as Dr. E. Albert showed. Apart from the abnormal dispersion, the dye molecules do not vibrate at the point of absorption, but vibrations are destroyed and in return heat or chemical decomposition of the dye is generated.

One could now assume a chemical decomposition of the dye, the decomposition products of which only have a secondary effect on the silver bromide (€). However, this view was already recognized by Prof. H.

W. Vogel as not generally applicable ').

In my opinion, the effect of the bromide silver and the dye increases each other, regardless of the light sensitivity of the dye for itself.

The bromide silver combines with the dye through Molecular Attraction ®) and is colored. The added dye would by itself strongly absorb light at the point of the absorption strip and be converted for the most part into heat, but only to a lesser extent (because most of the sensitizing colors are fairly lightfast) into chemical work (oxidation). The loss of light in the first case I recommend "photothermal extinction", those: in the latter case to be called "photochemical extinction"). Silver bromide, etc., intimately mixed or combined with a suitable dye, has the effect that a large part of the light now absorbed by the dye is converted into chemical work, with the silver bromide being involved

is drawn into the process. The tendency of the dye to oxidize in light ®) is supported by the property of bromide silver to give off the deoxidizing bromine in light.

If, in the case of colored substances with strong elective absorption, there is a photochemical process in addition to the conversion of the light into heat, then in the latter, too, the rays of light of the wavelength that cause the former come into action. The position of the absorption strip of the dye remains unchanged, since light rays of the same type are sometimes converted more into heat, sometimes more into chemical work; In quantitative terms, the absorption must then change by adding the "photochemical" to the "photothermal extinction", as Bunsen does with the mixture of chlorine and hydrogen (chemical and optical extinction) and Marchand with ferric chloride and oxalic acid showed. In all of these cases the maximum of the photochemical decomposition in the spectrum depends mainly on the position of the absorption strip of the colored component.

On the basis of the above facts I believe I am justified in formulating the following as a law for photochemical decomposition:

The photochemical extinction of a mixture is in many cases caused by the photothermal extinction of a component determined.

1) This is the view Abney expressed, based on his experiments with cyanine. Cyanine decomposes on its own in yellow. If you cover a glass plate with raw collodion, which is colored with cyanine and expose the spectrum, cover it with bromosilver collodion and develop without further exposure, an image appears at the areas hit by the yellow light, where the cyan blue the absorption stripe shows. Direct addition of color and subsequent exposure gave the same result (see my "Detailed Handbook of Photography", 1883, 6th issue, vol. II, p. 17).

2) Photographic Communications, Vol. XV, p. 91.

3) If one assumes that the dyeing of fibers (wool, etc.) is done by chemical connection with the dye, the same can be assumed here too; in the opposite case: molecular attraction.

4) To this is added the "photo-electric extinction" in certain electric processes brought about by light. The above designation seems to me to be more generally applicable and more precise than the Bunsen division into "optical" and "chemical extinction".

5) Or brominate yourself.

About the behavior of the haloid connections etc. 25

If the mixture (or the compound) of a colored body with a strong elective absorption capacity is decomposed with another in the light, the photochemical decomposition mainly involves light rays of the same wavelength as the former absorbed by photothermal extinction; thereby a maximum of the photochemical decomposition in the spectrum is determined by the colored body. If the body has a notable sensitivity to light with its lower elective absorption capacity, this decomposition in the light appears more or less characteristically in addition to that caused by the strongly absorbing dye.

By adding dyes to certain silver salts (especially bromine and chlorine silver), their sensitivity to the less breakable rays can be increased, according to Vogel's observation, so that the mixture is more sensitive to light than any of the individual rays

Components, whereby the maximum of the dye effect is based on the law mentioned above. Use of the colored silver bromide gelatin plates and orthochromatic plates.

Silver bromide gelatine plates which have been sensitized to any part of the spectrum by the addition of the above-mentioned dyes can find many uses; namely to study the spectral phenomena themselves, which up to now could only be photographed from the ultraviolet to the green part on silver bromide gelatine, but now with ease up to over  $C\ddot{A} \pm m$  Roth (for example with cyanine or iodine green), whereby with incomparably large This can be done more safely than with so-called "red-sensitive Collodion emulsions".

Furthermore, paintings, carpets and embroidery can be reproduced with the correct brightness value of blue and violet on the one hand, yellow and red on the other hand, without the former being bright, the

in the end appear dark, which is the greatest flaw in ordinary photographic preparations! I achieved this with silver bromide gelatine plates, which were colored with eosin, cyanine, rose bengal, aniline violet varieties (see pages 13 and 15), naphthalene red, although a yellow glass was placed in front of the objective to weaken the blue rays.

I presented such orthochromatic photographs at the end of August 1884

and, without having knowledge of the as yet unknown representation of Prof. Vogel's azalin plates; I presented a whole collection of very difficult to reproduce watercolors, embroidery, but especially of old yellowed oil paintings, which until now have presented almost insurmountable difficulties for the photographer, at the foundation festival of the Association for the Care of Photography in Frankfurt am Main on {1. September 1884. The first application for the study of absorption spectra is in the pre-

lying treatise has been described.

About the effect of various dyes on the behavior of the bromide silver against the solar spectrum. Of

J. M. Eder.

(Part I, presented at the meeting of the Imperial Academy of Sciences on December 3, 1885.)

In the previous treatise!) I described my investigations into the effects of the solar spectrum on silver bromide, silver chloride and silver iodine, both in the presence of dyes and in an uncolored state.

I named a large number of new photographic sensitizers for silver bromide, and determined the position of the maximum of the increase in sensitivity brought about by the dye in the less frangible part of the solar spectrum.

I continued these investigations and also considered the effect of such dyes on bromosilver gelatin which did not produce a clearly characterized maximum of photographic sensitization.

In the meantime, Messerschmitt's publication had appeared, which challenged the views gained up to now about the sensitizing effect of the dyes on bromide silver. Given the importance of the colored ("orthochromatically acting") silver bromide plates for the theory of the photographic effect of light, as well as for the practical application of the photography of appearances and paintings, I extended my work to include these controversial points.

For my experiments, silver bromide gelatine plates (made by means of the "ammoniacal process") were used, which were usually bathed in the dye solution. The concentration of the latter was mostly  $\frac{1}{100}$  /  $\frac{1}{1000}$  /  $\frac{1}{10000}$  ;; In individual cases, however, the concentration had to be taken 10- to 100 times stronger. The slit of the Spectrograph®) was used Similar to 0.04 mm; the exposure time in direct sunlight varied from 3 seconds to 20 minutes

sufficient patience, the concentration of the dye and the exposure time of the individual dyes

1!) Comp. pag. 1 of these treatises. ?) From bromammonium, gelatin and ammoniacal silver nitrate solution (see p. 9 of these papers). ?) I used the Steinheil's large spectrograph, which I referred to on p.5 of these papers.

About the effect of various dyes, etc. Di.

it is found that many dyes on silver bromide gelatine are photographic (so-called "optical") sensitizers, which would be declared ineffective for superficial samples.

At the moment I can explain on the basis of my very numerous experiments that it is a very general property of dyes to have a sensitizing effect on silver bromide (and silver chloride), i. H. to increase the sensitivity to certain colors of the solar spectrum, to which uncolored ones

Bromide silver is not or only slightly sensitive.

Red and orange-yellow dyes derived from azo-naphthol or related compounds (oxy-azo dyes).

This includes many dyes which come on the market as "Ponceau species" <sup>1)</sup>. The dyes of this group, both in the solution and in the dry state, lack that intense absorption band in green (or yellow) which characterizes the "eosin colors" so much. The absorption spectrum of those colors is mostly a one-sided (from violet to green) or there are very broad absorption stripes in green and blue, which gradually become weaker towards violet. |

If you dye bromine silver with these colors, the light sensitivity of bromine silver for spectral green and yellow is increased in most cases, without this effect increasing to a clearly limited maximum, which corresponds to the broad absorption band.

Echtroth (sulfonic acid of naphthalene-azo- $\beta$ -naphthol). If an Elena is bathed in an aqueous solution of this dye for a few minutes (concentration 1: 1000 - 10000), the sensitivity of the bromide silver increases to beyond the Fraunhofer line D of the solar spectrum to orange. One notices in a photograph of the solar spectrum obtained with such plates: 1. the spectrum image, which always occurs normally on bromosilver gelatine, from ultraviolet to towards the Fraunhofer line E?) And 2. then a weak effect in green and yellow, which between E and D an indistinct maximum

reached (see curve 1 in bias) With longer exposure, the effect of the green and yellow light comes into its own, as the dotted curve indicates

Xylidin-Ponceau?), For the production of which xylidine derivatives are used in addition to naphthol, sensitizes bromosilver gelatine to the less breakable rays in a similar way to the previous one. If the dye quantity is considerable, a small maximum appears as in curve 1. With small amounts of dye, only a weak, even sensitization from E to above D is noticeable, as the solid curve 2 shows.

Anisolroth (anisole-azo- $\beta$ -naphthol sulfonic acid) behaves similarly; the photographic effect of the solar spectrum extends over D into orange.

The same applies to Ponceau 3X (sulfonic acid of benzene-azo-benzene-azo- $\beta$ -naphthol)

also from Neuroth (from Kalle in Bieberich, combination of amidoazobenzene sulfonic acid with Schäffer'scher  $\beta$ -naphthol sulfonic acid<sup>®</sup>), from

1) cf. Fehling's "New hand dictionary d. Chemistry", Vol. IV, p. 625 and p. 641. Benedict: "The artificial dyes", 1883, p. 204.

2) I have reproduced the normal photographic image of the solar spectrum on ordinary (not colored) bromide-silver gelatine on page 8 of these treatises. It always appears on colored bromide-silver plates; only in the latter case there is a further increase in photographic sensitivity which is peculiar to each dye and which can be ascribed to the dye effect.

3) From poorly soluble  $\beta$ -naphthol sulfonic acid with xylidine; Sodium salt.

4) I am grateful to Dr. Hoffmann (KeallrerineBieberich's factory).<sup>4</sup> \*

28 J.-M. Eder.

Crocein 3Brx (from easily soluble naphthol sulfonic acid with naphthylamine!) Acid orange (from diazobenzenesulfonic acid and  $\beta$ -naphthol?) And

Crocein orange (made from poorly soluble  $\beta$ -naphthol sulfonic acid and diazobenzene?). The tropaeolins generally do not show any pronounced sensitizing effects

Bromide silver. A very strongly tinged variety, the dimethyl orange, increases it a little

Sensitivity to yellow. and green. On the other hand, "nitrated tropaeolins" are noticeably beneficial.

== = =: es a <m m oO & jew)>

1. Spectrum picture on silver bromide gelatine colored with Ponceau species. - 2. The same.  $\hat{\epsilon}$  "3. Colored with violet from paraoxybenzaldehyde with dimen-

thylaniline.  $\hat{\epsilon}$  "4. With hydrochloric acid diazoamidobenzene.  $\hat{\epsilon}$  "5. Chrysaniline.  $\hat{\epsilon}$  "6. Poirrier $\hat{\epsilon}$  "™ s blue.  $\hat{\epsilon}$  "7. Neutral purple. - 8. Helianthin.  $\hat{\epsilon}$  "9. Naphthol blue or neutral blue.  $\hat{\epsilon}$  "10. Violet from acid fuchsine with benzyl chloride.

Such nitrated tropaeolins are keelrantchin $\hat{\epsilon}$  and jasmine (Geigy, which are soluble in alcohol. Small amounts dissolve in water. Both are yellow and take on a darker shade with ammonia. Curve 8 shows the effect of helianthin (Fig. 15). It "increases:" the sensitivity "from bromosilver gelatine to over D .. The dye effect is closely related to the normal spectrum image on bromosilver and grows between D and B = 7 to its = fairly broad It is noteworthy that the absorption spectrum of a helianthin-colored gelatine film does not have an analogue absorption band, but rather absorbs the blue end towards green on one side. The addition of ammonia increases the sensitizing effect of the helianthin. Jasmine behaves in a similar way, which sensitizes in particular to green; however, the sensitizing effect expands with longer exposure - to: over: D, without me Maximum observed.

Another orange dye: "Toluidine, diazotized with"  $\alpha$ -naphthylamine "(from Dr. Johann Walter), |behaves similarly to the Ponceau species;

Ammonia works favorably. The small maximum between E and D is closer to D than with Curve 1; a weak, even effect runs from there into the red to above C.

Crocein-scarlet fever (combination of amidoazobenzenesulfonic acids with  $\beta$ -naphthol-"sulfonic acid) and other" croceins "also show a similar behavior. All the orange-yellow to red azo:

Dyes increase the light sensitivity of the bromide silver for green and yellow rays around the piece

1) Received by Dr. Walter. 2). Like previous: 3) Like previous.

About the effect of different dyes etc. 29

from E to D and beyond, with this effect directly following the light sensitivity of ultraviolet to E, which is peculiar to bromosilver, without any between

both would have a place with insufficient sensitivity to light! '). Red-violet dyes from aniline red.

From acid fuchsin (fuchsin S), that is rosaniline sulphonic acid, a violet-red dye is obtained through the action of benzyl chloride, which shows the absorption band in the spectrum further towards orange than aniline-red?). The same  $\epsilon$  applies to the dye from acid fuchsin with bromomethyl. Both dyes, which I received from Dr. Walter received, did not tend very strongly and were therefore used in solutions of about 10<sup>-4</sup> rank!. The photographic effect of violet from acid fuchsin with benzyl chloride on bromide- silver gelatine plates is shown in Curve 10. This color increases notably (especially with a little ammonia) the sensitivity of the bromide silver for green, yellow to orange; at D (a little further towards orange) there is a moderate maximum of the sensitization and a weaker continuous effect connects this with the normal spectrum picture on bromide silver. The dotted curve shows the effect with a shorter exposure. Just like this dye, the violet dye from acid fuchsin sensitizes with bromomethyl, which is also purple-red and gives the bromide silver gelatine a good light sensitivity for yellow and orange. Both dyes

cause an increase in the sensitivity of the bromide silver to over C. after longer exposure. Carmine.

Carmine in ammoniacal solution is not so noticeably sensitive to silver bromide gelatine. as on bromosilver collodion. I observed it when using concentrated dye solutions

but after a few unsuccessful attempts an increase in the sensitivity of the bromide silver gelatine to green. So here too there is no significant difference in behavior between silver bromide gelatine and

-Collodion against this dye. Brazilian.

The Brazilian?) Gives a deep red color in a weakly ammoniacal, aqueous solution, which strongly absorbs the green of the spectrum. If strongly colored baths are used, the sensitivity of the colored bromide silver gelatine plates to green and yellow increases. The sensitization extends weakly and fairly evenly from E (following the spectrum image on bromide silver) to D1 /, C (similar to Curve 2). If the color is strong, a weak maximum of the sensory

bilization near

D. Alo<sup>o</sup> £ &  
purple,



represented by heating also & with nitric acid, dissolves in ammoniacal water with purple color. It sensitizes bromosilver gelatine evenly but weakly for green and green-yellow up to D (roughly in the same way as Curve 2 indicates). This dye works only in larger ones

Concentration. I could not notice the occurrence of a clear maximum of sensitization.

1) The latter case can be observed with certain eosin colors and naphthalene red, which I pointed out earlier.

2) cf. p. 15 of these treatises. "It should be noted that an aqueous solution of rosaniline mixed with a little ammonia also sensitizes for yellow-green to orange.

3) I obtained crystallized Brazil from Dr. Schuchardt in Görlitz; it is the dye of the brazil or sapan wood.<sup>30</sup> J.M. Eder.

Various purple and blue dyes.

Violet from toluenediamine, by Dr. Walter after the "Lauth's reaction" is a notable sensitizer to orange, while the common violet Lauth's in my hands did not give favorable results. The sensitizing effect of the former reaches up to C and is quite similar to that of the methyl violet, of which I gave the effect curve in my earlier treatise (p. 13).

Victoria blue<sup>°</sup>), which shows a strong absorption spectrum and quickly fades in light, gave me no favorable results. Ethylene blue and phenylene blue, from which I also expected good results because of their strong absorption, did not show any good effect as a photographic sensitizer for silver bromide. |

Paraoxybenzaldehyde dye.

A dye (manufactured by Dr. Walter) from paraoxybenzaldehyde and dimethylaniline dissolves in alcohol with a green color and fluoresces strongly red. The weakly acetic acid solution makes the silver bromide slightly red-sensitive. |

The slightest trace of alkali colors the solution deep purple and it then gives a strong absorption band in the yellow. If the alcoholic solution of the dye is added to weakly ammoniacal water (! /; "2° /, ammonia) and bathed in silver bromide plates, the sensitivity increases notably for green, yellow and orange. In the case of E, the sensitizing effect is closely related to the usual photographic effect on bromide silver and runs evenly up to C and under favorable circumstances a broad sensitization maximum between C and D can be seen in the solar spectrum "œ from (see curve 3).

The dye works quite cheaply and should not be used in concentrations that are too low become.

Green dye made from toluene aldehyde.

One of Dr. J. Walter made dye from toluic aldehyde in dimethylaniline increases the sensitivity of the bromide silver gelatine to the less refractive rays n of the spectrum. With ample exposure, the effect extends weakly and evenly from E to over B and shows us a slight maximum in orange (C! /, D), not

unlike methyl green (see my earlier essay, p. 13 ). | | Adding ammonia does not change the green color of the solution; the sensitizing effect

But then bromide silver emerges more clearly. Neutral purple.

The neutral violet shown in the von Gans paint factory in Frankfurt shows in colored gelatine foils a one-sided absorption of the spectrum from violet beginning with all the blue, green and yellow and the beginning of the orange. The absorption ranges (with strong coloring) up to 582 or 90 nm wavelength.

1) On the Lauth's reaction, see "Annual Reports on the Advances in Chemistry" for 1876, p. 1185 and for 1883, p. 1799. |

?) Made from p-phenylenediamine.

>) Made from tetramethyldiamidobenzophenone and  $\alpha$ -phenylnaphtylamine (Dr. Walter). About the effect of various dyes etc. al

A silver bromide gelatine plate colored with it experiences an increase in sensitivity for green, yellow, orange and red. The photographic image of the solar spectrum extends from ultraviolet to over B in red with very abundant exposure; from the Fraunhofer line E the effect will be noticeably less, but from then on it still runs strongly and evenly to B (see curve 7). This dye can therefore be useful in the photography of the spectrum, but only gives a sufficiently strong drawing of the lines in yellow and orange with ample exposure. I:

I recommend using it as an aqueous bath for silver bromide gelatine. Crystal violet!)

acts similar to methyl violet 6B. It increases the sensitivity of silver bromide gelatine to orange with a maximum at C! /, D (see my earlier treatise, p. 13).

Poirrier's blue.

This dye, which was also recommended as an indicator for titrating with acids?), Dissolves in alcohol with a beautiful blue color; a trace of hydrochloric acid makes the color more intense. This solution, mixed with plenty of water, serves as a bath for bromide silver plates. As a result, these become insignificantly more sensitive to all less refractive rays. In my experiments, however, there was nowhere a maximum of sensitization, but the effect was rather weak and extended

evenly into the Roth (against DB). This effect is shown by curve 6 in

FIG. 15. Hydrochloric acid diazoamidobenzene.

Mr. Messerschmitt mentions of this dye that it has a uniform absorption which extends over larger parts of the spectrum from the violet end. In spite of the fact that it does not show an absorption maximum, nevertheless a sensitization maximum appears in the yellow (between Drundeb).

He "also" sought this body (obtained from Dr. Schuecharded, and stained my silver bromide gelatine plates with its weakly ammoniacal solution. The photographic record of the solar spectrum showed that the photosensitivity had increased notably for green and yellow. The effect was up to into green (E? /, D) very intense and with longer exposure extended intensely to over D against CU into orange (see Curve 4, Fig. 15; the dotted line represents the spectrum image on uncolored bromosilver gelatine The occurrence of a sensitization maximum could not be noticed anyway.

I do not want to doubt Mr. Messerschmitt's information, however, since the chemical preparations can be different and because I myself observed a similar case on the helianthin, where the dye absorbs evenly (without an absorption maximum), but still shows a weak maximum of sensitization.

Chlorophyll,

which is a good sensitizer for Roth in the case of bromosilver collodion (according to Becquerel, Cros, Vogel,

Ives), is very unsafe with silver bromide gelatine; namely, the alcoholic solution penetrates them

t) Made of chlorocarbon oxide (Geigy). 2) Chemisches Centralblatt, 1885,

p. 758.32 | 2M = Edier

Gelatin and almost does not work. Nevertheless, I found it effective in the latter case as well. Through continued experimentation, I have come up with a staining method that will almost certainly allow chlorophyll to be used on silver bromide gelatin.

You extract ephey leaves with warm alcohol. An alcoholic chlorophyll solution that is as concentrated as possible, produced in this way or in another way, is poured into weakly ammoniacal water. After adding 10-20% of the alcoholic solution, the water should be very green in color. The alkali gets the chlorophyll dissolved in water. Although this solution absorbs the red light less strongly than the original alcoholic chlorophyll solution, it is more suitable for bathing gelatine plates. If the Chlorophylli solution was sufficiently concentrated, one notices a clear increase the sensitivity to green, yellow, orange and red. In some cases the sensitizing effect of Chlorophyllis appeared in close connection with the usual spectrum image on bromide silver and ran weakly and evenly up to B in the red. |

In other cases a weak maximum of sensitization occurred between 3 and C and a second between C and D, similarly. like it from Becquerel and Cros!) with bromide silver collodion

was observed.

Naphthol blue and neutral blue.

Naphthol blue (obtained from Dr. Schuchardt in Görlitz) and the neutral blue from the Frankfurter Anilinfarbenfabrik (Gans & Co.), which may be identical to it, dissolves slightly in water with a dark purple-blue color and does not change afterwards Addition of ammonia. It is not the same as idophenol?). Naphtol blue is a good sensitizer for the less refractive rays of the solar spectrum. I use it in an aqueous solution 1: 3000 to 1: 10000 with the addition of ! /, Å € "2Å ° /, ammonia as a bath for silverbromide gelatine plates.

Without ammonia, the sensitizing effect of this dye is much less.

The sensitizing effect is felt over all the green, yellow, orange and the visible red of the solar spectrum. With sufficient exposure, the photographic effect is strong from ultraviolet up to the Fraunhofer line E, from then on it is weaker, but very clearly and evenly up to the line A in the red. At C the effect rises to a broad, not very excellent maximum (give)

If the blue and violet rays of light are kept in front of the slit of the spectrograph by advancing a red glass (€) or an aqueous solution of chrysoidin \*), one obtains a much clearer photograph of the red part of the Solar spectrum and the image extends over line A in the most visible red, yes, it seems, to infrared.

Naphthol blue surpasses chlorophyll, which also sensitizes bromosilver gelatine to red, significantly in terms of the power and intensity of the photographic effect in red, but unfortunately mostly gives veiled plates.

Working with such plates requires a lot of caution. I use a dark red lamp which is set up so that no direct lamp light hits the plate. But it is better to put some brown tissue paper over the red glass and do the whole work of bathing as much as possible

to finish in the dark. You can safely perform these simple operations by just touching them

1) S. Eder's "Detailed Handbook of Photography", 1885, Part II, p. 17.

2) In Fehling's "New Handwritten Dictionary of Chemistry" (Vol. IV, pag. 627 and 661) both dyes are declared to be identical.

3) Copper oxide glass lets through only the red and orange and part of the yellow rays.

4) The chrysoid solution is placed in front of the gap in glass tubes. It strongly absorbs ultraviolet, violet, and blue; the yellow-green, yellow and red rays, however, allow this dye to pass through with little weakening and therefore it is particularly suitable as a screen for the spectrophotography of the less breakable rays starting from the line E.

About the effect of different coloring agents etc. | os

quit. The plates must be dried in absolute darkness. A very weak red light is sufficient when inserting it into the cassette. The course of development is followed at times in a red light; now the cup is covered completely.

The developer is the pyrogallol potash developer!) With the addition of a few drops of potassium bromide solution (1:10) per 100 cm<sup>3</sup> Developer.

For orthochromatic photography of oil paintings, I don't have any naphthol

blue yet get satisfactory results.

Quinoline yellow.

I received the quinoline yellow<sup>2)</sup>, which the Berliner Farbenwerke represent, from the Scheringosche Chemische Fabrik. The same thing shows a strong absorption spectrum in the blue and therefore I expected an increase in sensitivity in the blue.

The effect was not very good, however. However, the blue between G and F was more pronounced (corresponding to the absorption band), but the sensitivity to violet and ultraviolet rays decreased.

It struck me that this dye made the brambles very sharp and clear

Caused lines in the spectrum image and prevented the creation of so-called

Liehthöfe. Indifferent dyes.

There are many dyes which only cause a weak and some which do not cause any photographic sensitization of the bromide silver and still have a clear influence on the formation of the photographic image on bromide silver gelatine, namely where the normal, peculiar to the bromide silver photosensitivity is present; d. i. especially indigo blue, violet and ultraviolet.

Such dyes cause the Fraunhofer lines so appear harder and clearer (similar to anisole yellow) and generally that the plate stays clear in the developer. Such dyes are, for example: the "extra para blue" and the "? I blue" from Master Lucius' paint factory; Both reduce the sensitivity of the bromide silver to light, but the favorable photographic effect, in terms of the purity of the lines, emerges from the ultraviolet to the green.

Many orange and yellow dyes have a similar effect, both sensitizing and non-sensitizing. They prevent the creation of halos; for example, they also make the clouds stand out better in the sky when taking pictures outdoors. This secondary effect also appears, for example, with eosin and chrysaniline etc., which are also sensitizers for yellow and green, but I don't think that the sensitizing effect of the dyes has anything in common with this phenomenon. The lateral scattering of the light?) Within the layer or the too deep penetration of intense amounts of light is probably reduced.

According to Messerschmitt \*  $\hat{a} \in \infty$ ), quinine sulfuricum is supposed to increase the sensitivity to whitelight and to ultraviolet, and Messerschmitt suggests that this is also the case

the fluorescence of quinine. According to my repeated attempts, quinine has no effect

1) See page 7 of these treatises, as well as my "Handbuch der Photographie", III. Vol.

2). The alcohol-soluble quinoline yellow is made from phthalic acid and quinaldine; the water-soluble is the sulphonic acid of the previous compound.

3) So-called "molecular dispersion" or "molecular irradiation" (cf. Eder's "Handbuch der Photographie", Vol. II, pag. 54, in which the irradiation and lateral extension of the photographic image are dealt with in detail ).

#) Annal. d. Physics and Chemistry, New Series, Vol. XXIV, 1885, pas. 07.24 J.M. Eder.

as a bath of the bromide-silver gelatine plate (before exposure) or as an additive to the molten emulsion (which J. Plener had also tried without success). In dilute solutions it does not change the sensitivity to light; in concentrated form it even diminishes it. Messerschmitt's, too

â € § Bathing declared beneficial after exposure and before developing was useless

(see below). About an alleged abnormal effect of the photographic sensitizer:

chrysaniline.

In his treatise: "Spectrophotometric investigations of some photographic sensitizers" writes Messerschmitt!) About an alleged abnormal effect of chrysaniline on silver bromide gelatin: If the spectrum is photographed on a silver bromide gelatin plate colored with chrysaniline, a strong sensitizing effect appears in the Green (up to D), which follows the usual spectrum image on bromide silver \*). But if you take a spectrum image on an uncolored bromide silver plate, then bathe it in a chrysaniline solution (1: 20000) and develop it, the same effect should be achieved (according to Messerschmitt). "This is very remarkable," concludes Messerschmitt, "since there can be no question of a sensitizing effect on an uncolored plate." This statement is of decisive importance for the theory of the sensitizing effect of dyes on bromide silver. It shakes the foundation of the previously given theories of this phenomenon, which are based on the changed light absorption in the colored bromide silver and according to which the dye must already be present during the light effect. So I repeated Messerschmitt's experiment; alone always with negative results. FIG. 15 (solid curve 5) shows how the solar spectrum acts on the silver bromide, which has been colored with chrysaniline before exposure, when the photographic image is produced as usual. There is a strong sensitization in green (at E), which connects to the usual bromide silver image as an intense band. At the same time, the sensitivity to violet and ultraviolet decreases.

If, however, the solar spectrum is photographed on uncolored bromide silver plates, bathed in chrysaniline solution and then evoked with the development of iron oxalate, a spectrum image of a completely normal type develops; it hardly differs from a photograph of the solar spectrum on quite ordinary bromide-silver plates with the usual evocation. You only notice that the image becomes visible more quickly when it is evoked (developer) and that it extends a little further towards green and a little further into the ultraviolet (see dotted Curve 5 in Fig. 15). There is no sign of a strong, well-characterized band of awareness.

This phenomenon is exactly the same (only weaker) as when bathing the exposed plates before the evocation in ve Thin hyposulphurous sodium bicarbonate (1: 10000) or silver nitrate. These means only increase the overall sensitivity of the bromide silver?) Or the speed with which the image appears in the developer is promoted. An actual, sharply characterized increase in color sensitivity is not associated with this. |

Eosin and other red dyes have also been added to the developer fluids; however, an increase in color sensitivity is never achieved and is in no way intended. These dyes are only intended to cover any existing yellow coloring of developers and thereby make them easier to sell in stores; or you want to make the developer liquid impermeable to actinic light in order to prevent haze.

')} Annal. d. Physics and Chemistry, New Series, Vol. XXV, 1885, p. 689.

Srklerr Messerschmitt also mentions the identical statement made by me earlier (p. 16) about the spectral behavior of the chrysaniline-colored bromide silver.

?) Not always strong and with some types of silver bromide gelatine this effect does not occur at all. About the effect of different dyes etc. 35

Thus, this experiment also decides in favor of the "absorption principle", because the dye has a completely different effect if it is present in the bromide silver during the light effect and

absorbs light as if it did not act until after exposure ').

About the connection between the absorption of dyes and their photographic sensitizing effect. Determination of the wavelength for the maximum effect.

It is well known that the "sensitizing" dyes, which show an absorption strip in the spectrum, cause the same locally corresponding increase in the light sensitivity of the silver bromide which is colored with it. Furthermore, it is a fact that there is never an exact coincidence of the absorption strip of the colored gelatin film with the place in the spectrum where the color sensitivity is increased. Prof. Vogel made this statement.

I myself compared the absorption of colored gelatine foils and the sensitization maxima on the correspondingly colored photographic plate and in my earlier treatise (p. 20) the difference between the absorption maximum in gelatine and the sensitization maximum on bromide silver was  $16 \pm 20$  nm.

Wavelength set.

In the "Spectrophotometric investigations of some photographic sensitizers" by Messerschmitt(?) There are manifold points of contact with my earlier published investigations on the same subject.

The numerous precise determinations made by Messerschmitt of the light absorption of eosin, cyanosine, methyl eosine, fluorescein, cyanine, chrysaniline, diamidoazobenzene, which are of high value for the knowledge of the absorption ratios of these substances, are not discussed here. |

On the other hand, it is of interest for the present investigations that Mr. Messerschmitt found the difference between the middle of the absorption of the colored gelatine foil and that of the sensitization to bromide silver:

With eosin. . . 29 nm wavelength |  $\pm 6$  nm. Cyanosine.  $\pm 3$

This agreement with my statements is therefore a satisfactory one.

Nevertheless, I subjected the absorption ratios of some dyes in the dissolved and dry state (colored gelatine foils) to a more detailed examination and compared them with the photographic sensitization of bromosilver gelatine caused by them. The center of the most intense absorption bands and the center of the photographic maximum effect were measured in yellow, orange or the like and their position in the spectrum was reduced to a millionth of a millimeter wavelength. This measurement is most accurate when the dye shows a narrow, intense absorption band, which usually results in a narrow band of sensitization in the photographic image of a colored bromide silver plate.

The results of these determinations are summarized in Table I.

If the dyes do not show a narrow absorption band, this is the absorption spectrum

one-sided, that is: if you completely absorb one half of the spectrum, that is the comparative one

t) I tried a few other dyes in the same direction, but none of them produced any effect as sensitizers when placed on the plate after exposure and I therefore did not continue these experiments. |

2) Annal. d. Physics and Chemistry, New Series, Vol. XXV,

1885, p. 655, Sn

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Determination of the location of the light absorption of the color and the sensitizing effect on the bromide silver

plate a much more difficult one. With increasing intensity (concentration) of the dye solution that moves

Middle of the difference 5 nr E maximum of the E ne (expressed in millionths of a millimeter sensitization of the absorption wavelength) n fedeneskenen maximums of the ee dye in applied dyes ee colored BelatÄ ± nz Se and of the ki acensensitization solution ERWNE Aqueous eelatimetolie maximums of the solution (density colored (density of (=) (density of || of bromide silver bromide alcohol \_ gelatine 053) - 0.849) - 1'326) eosin, yellowish (tetrabromofluorescein - sodium) er 929 922 930 60 10) eosin, bluish (tetraiodofluorescein sodium) 320 922 940 869 de fluorescein and ammonia 499 488 499 027 U. =

28 cyanosine. 002 943 990 578 AO) Naphthalene red 69 as 932 980 d = 18 cyanine. 990 95 90 613 dB |

Methylerythrin 046 70 de == 2A Crystal violet Sr 999 626 de 2 Gentian violet RR with ammonia. 999 630

deal] aniline red 960 974 dt toluidine red. o61 980 1 3, methyl violet. 995 626 | Anisolroth 922 950â €

"5960 â €" 28â € "98 Echthroth Se 490 (9) 900 de 09 Fluorescein, alkaline (still wet) 499 | 027 dr 28 Bleu fluorescent 613 660 a violet from acid fuchsin and benzyl- | eNlorider, en 074 097 de 23 Violet from paraoxybenzaldehyde and dimethylaniline 6130) 660 (?) A A Saffranin 643 (?) 60 AN Corallin 062 889 =solid green. 639 650 di == ii

The absorption band continues to widen and also the limit of a one-sided even sensitization is difficult to determine on the photographic plate. I roughly determined the limit of the intense absorption spectrum and the limit of the strong sensitization of the colored photo- graphic plate and found the numbers given in Table II:

About the effect of different dyes etc. a



Table II. || Difference photographic of the limits of absorption of the colored sensitization of the absorption gelatin film colored of the dye and applied dyes (Expressed in millionths of silver bromide gelatin | of the millimeter wavelength) from ultraviolet sensitization of the up colored bromide silver ee een eun absorbed Roth, Orange, yellow, gradually weakening against green; special- Neueraldlau a ders to 656 â € "500 764â € " 770 (?) enssanÄ ± In ame. from purple to 510 540 | d = 30 helianthin -. 2-2 = â € œfrom purple to 510 or 520 | 590â € "630 Hydrochloric acid diamidoazobenzene | and ammonia = rn from violet to 908 074 dd neutral violet. . 2 2 ... || from blue to 582 or 590 670 dâ € "80

So the sensitization maximum in colored bromosilver gelatine emulsion is always a certain amount further towards Roth than the absorption maximum in colored gelatine sheets. One must assume that the reason for the difference is that this effect is due to the greater density and the greater refractive power of the bromide silver, which includes the dye (cf. the density of the media examined by me in the table D). Since I had also proven (p. 19) that the bromide silver itself absorbs the dye, the phenomenon described would probably be adequately explained.

Herr Messerschmitt, however, complains in his repeatedly mentioned paper that it has not yet been established experimentally whether the silver bromide, conceived as a colored medium, actually causes this displacement of the absorption strip. Now to remove these doubts about this,

I examined the absorption spectrum of the colored bromide silver. Absorption spectrum of the colored bromide silver.

The investigation of the same is not easy to carry out, because the bromide silver must be produced under the same conditions as it occurs in the photographic plate!). In the presence of gelatin, the silver bromide must therefore be represented in the form of an emulsion and separated from the gelatin solution using Plener's centrifugal machine (see my earlier treatise, p. 19). All the work must be done in total darkness or by ruby red light.

For the coloring of the bromide silver I chose eosin because it gives an intense absorption band and a sensitization maximum, the position of which is relatively easy to determine.

The silver bromide, colored with eosin and then thoroughly washed by centrifugation, is rose-red. It is extremely sensitive to light. The red color disappears in the sunlight

in a few seconds; it must therefore be kept in absolute darkness.

1) The silver bromide precipitated from aqueous solutions as well as the silver bromide obtained from Collodion emulsion shows a different absorption spectrum in the blue; therefore I did not use it in my experiments, since I was using bromosilver gelatine emulsion.

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The examination of the absorption spectrum of the same in daylight must therefore be carried out with the greatest possible speed and on frequently changed samples. The bromide silver was spread thinly on a glass plate and brought wet or dry in front of the spectral apparatus.

In the absorption spectrum of the The absorption band of the eosin is clearly recognizable, only it is shifted further towards the red end of the spectrum than is the case with the pure dye or with a gelatine foil colored with it: Curve in Fig. 16 shows this shift.

The center of the absorption band is  $562 \pm 564 \text{ \AA}$ . Wavelength, that is at the point where the center of the increased sensitivity of the photographic eosin - bromide silver plate ( $= 563 \text{ nm}$ ) lies.

The optical absorption of the yellow-green rays of the spectrum by eosin bromide coincides with the position of the maximum of sensitization. |

Firstly, this provides evidence that the bromide silver (conceived as a colored medium) shifts the absorption stripe of the dye very strongly towards Roth and, secondly, it is shown that the absorption maximum is exactly at that point. falls where the maximum of sensitization lies.

The examination of the absorption spectrum of the eosin bromide silver shows another interesting result: the bromide silver (as it is contained in the highly sensitive gelatine emulsion) shows a light absorption which

encompasses the entire spectrum of the sun and is strongest

a) Absorption of the spectrum due to eosin in the blue part of the spectrum. In the presence of colored bromide silver.  $\pm$  b) Absorption through with eosin

a eosin bromide shows the colored gelatine associated with eosin.

To widen absorption strips according to both Roth and Green by gradually connecting absorption shadows on both sides. The latter may well be the key to the phenomenon that

a photographic weak effect can be traced surprisingly far.

## Conclusions.

These results and the numbers given above are relevant to further conclusions. Namely, they show:

1. That neither the absorption spectrum of the alcoholic nor the aqueous solution of the dye or the dry colored gelatine film coincides with the position of the photographic sensitization maximum on colored bromide silver gelatine. This is new evidence of this previously accepted fact.
2. The sensitization maximum of the colored bromide silver is further towards Roth than the absorption maximum of any of the solutions investigated.
3. The density of the bromide silver ( $d \approx 63583$ ) is compared to that of the gelatine ( $= 1vS26s028r0ss$ ), that the greater density of the refractive agent is probably the reason. this shift can see. Although the "Kundt's Law" shows very many exceptions, "there is still a great deal of regularity in these special cases. ?
4. The position of the absorption maximum of the dye (in gelatine) and of the sensitization maximum on colored bromide silver in the spectrum differ fairly regularly on average by 30 wu.

') For example with aqueous and alcoholic solutions and in many other cases, as H. W. Vogel showed. About the effects of various dyes, etc. 39

Wavelength. That means: those rays of light which photographically most decompose the colored silver bromide at the point sensitized by the dye have an average wavelength of 30 or less than those which are produced by the colored gelatine (without silver bromide) be absorbed.

5. The absorption spectrum of eosin-tinted silver bromide and the maximum of the photographic sensitizing effect of eosin on silver bromide coincide completely. That means: those light rays which are absorbed by the eosin-containing bromine silver have the same wavelength as those for which the colored bromine silver shows the increased photographic sensitivity.

6. Deviations from the absorption spectrum of colored gelatine foils from the photographic spectrum image on the similarly colored bromide silver should not be regarded as exceptions to the "principle of absorption", because the absorption spectrum of a colored medium never allows a reliable conclusion the absorption spectrum of another equally colored medium.

If one divides dyes, which sensitize, into several groups (as recommended by Messers chmitt), the following overview results:

I. Dyes which gradually absorb the spectrum from the violet and whose sensitizing effect closely follows the usual photographic effect without a maximum). This category includes: soluble Berlin blue, Poirrier's blue, aniline blue, chrysaniline, various types of Ponceau, turmeric, neutral violet, chrysoline, diazoamidobenzene, jasmine, acidic orange, sometimes neutral blue and others. |

Furthermore, with some of the sub 2 mentioned dyes, the maxima appear at certain degrees of concentration and exposure times Sensitization So weak that they are barely or not at all recognizable.

2. Dyes which show an absorption strip in the spectrum and a sensitization maximum that has been shifted according to Roth. Eosin colors, cyanosine, methylethythrin, phloxine, rose bengal, aniline red, naphthalene red, cyanine, resorcinol blue, coralline, bleu coupier, safranine, methyl violet, acid violet, methyl green, acid green and some types of Ponceau belong here.

In the case of many of these dyes, the maximum sensitization and the usual photographic spectrum image on silver bromide are linked by a coherent, uniform photographic effect. This is most noticeable with methyl violet, aniline red, some violet dyes from acid fuchsin, but especially with neutral violet, naphthol blue and neutral blue.

The silver bromide dyed with naphthol blue or neutral blue (in the form of silver bromide gelatine plates) has the greatest qualitative sensitivity of all known photographic preparations to light of various wavelengths; the light sensitivity ranges from 360 - 760  $\mu\text{m}$ , wavelengths without interruption. This kind of sensitization of the bromide silver, discovered by me, is most suitable for the photography of the less breakable light rays (starting from the outermost Roth), however it is also very suitable for the photography at the blue end of the spectrum, as well as of the ultraviolet.

This body has a qualitative light sensitivity, which not only includes the color sensitivity of the retina of the human eye, but also includes the ultraviolet.

Some of the sensitizers that I have discovered can be used either on their own or mixed with eosin, etc., for "orthochromatic photography," for which the necessary indications are given in the present paper. |

After all, it is a pleasant duty for me, those gentlemen who support me in my work by kindly sending test materials to express my thanks. It is this

1) Apparent exceptions are only made by one or two dyes, which sometimes show a maximum within the closely related effect without otherwise showing a deviating appearance (see point 6).

40 J. M. Eder, on the effects of various dyes etc.

especially the factories of Geigy, Monnet, Gans & Ce. Kalle, as well as | Dr. Joh. Walter my investigations greatly benefited.

In general, the present investigations prove the absorption theory first set up by Prof. Vogel, taking into account my additions, to be completely correct. If you summarize everything, the following law results for the sensitizing effect of dyes on bromide silver:

Many dyes have a sensitizing effect on silver bromide (or chlorosilver), the increase in sensitivity to colored light being determined by the ability of the dyes to absorb the light. Those light rays which the colored bromide silver absorbs have the same wavelength as those for which the sensitized (colored) bromide silver shows the increased photographic sensitivity. A narrow or broad band of absorption gives the same for sensitization.

Certain dyes can increase the sensitivity of the silver bromide gelatine to the rays of light of longer wavelengths so that it changes from the extreme red without interruption

extends through the entire spectrum far into the ultraviolet.

About the effect of various dyes on the behavior of the bromide silver against the solar spectrum. Of

J. M. Eder.

(11th part, presented at the meeting of the Imperial Academy of Sciences on June 10, 1886.)

Following my previous work!) On the behavior of silver bromide against the solar spectrum and the influence of added dyes, I examined a number of dyes, focusing my attention on homologous or isomeric dyes and those as far as I could get them were included in the scope of my investigations.

In my brief preliminary note in the Wiener Akademie-Anzeiger on April 1, 1886, I mentioned the more important of these new sensitizers, the properties of which I will now describe in more detail. At the same time, I took into account the influence of the presence of potassium bromide in silver bromide, as well as the connection between absorption and sensitization and the importance of yellow or red screens in front of the spectral apparatus for spectral photography with colored and ordinary silver bromide Can.

The practical methods which result from this work for spectral photography, microscopic and astronomical photography are presented in a separate chapter dlung down-

be

placed.

Cerulein.

This dye, which is produced by heating bile with sulfuric acid, is very difficult to dissolve in common solvents; in alkalis it dissolves in green color. Cerulein sulfite (Cerulein.S), which is a double compound of cerulein with sodium bisulfite and dissolves in water, is more suitable. In an alkaline solution, cerulein makes the silver bromine much more sensitive to the less breakable rays (down to the extreme red). It is the best sensitizer for the rays in the region of the Fraunhofer line A, which I have come across so far and surpasses the naphthol blue in red sensitivity, as well as in the purity of the photographs; because

Naphthol blue easily gives rise to irregular reductions and haze.

1) cf. pag. 1 and 26 of these

treatises, 42 J. M. Eder.

To sensitize bromosilver gelatine plates with cerulein, I proceed as follows:

01 g of cerulein.S!) Are in 10 cm<sup>3</sup> Dissolved water and processed immediately. Mix 1â € "2 cm<sup>3</sup> this solution with 100 cm<sup>3</sup> Water and 8 drops of ammonia, bathe the silver bromide plates for 3–4 minutes and place them upright to dry \*). The solutions decompose quickly. The bathed plates still last a longer time (observation period 2 weeks), but seem to me better when they are fresh. These "cerulein plates" are sensitive to all rays of the spectrum from ultraviolet to above A (in red) and reproduce the lines sharply. It predominates, however, the light-sensitivity for blue and is also very great for violet and

ultraviolet, so that it is good to bring a dark yellow glass in front of the gap or a screen of chrysoidine when photographing the solar spectrum insert. I use an alcoholic chrysoidine solution (1: 12000), which is in a glass tub 11 mm thick. With an exposure of 90 seconds (up to 4 minutes) the Steinheil'sche Spectro-

graph (three flint glass prisms) a German

Lich image of the solar spectrum; of

3 A to D is the photographic industry

Approximately evenly, at D to Z

1. Image of the solar spectrum on bromide-silver gelatine colored with cerulein. It rises to a stronger effect

2. The same; with a chrysoidine screen in front of the column. 3. Typical spectrum image on bromide silver colored with diazoresorufin or bleeding; in blue is depending on the coupler.

Concentration of the chrysoid solution in

the glass tub a more or less broad minimum; Beginning at F or G, the spectrum with all its lines emerges again extremely sharply and extends to above O into the ultraviolet (see Curves 1 and 2).

Pyro-potash or pyro-soda solution with a little potassium bromide is used as a developer.

If a red copper oxide glass is attached in front of the slit of the spectrograph, the violet to green is very strongly attenuated and the spectrum appears very clear from approximately the Fraunhofer line D to Roth. There are even two lines in the infrared (Z and X?) With long exposure. However, blue and violet light also penetrates through the ruby glass, which is probably strongly weakened by the red glass, but not completely absorbed. Such glasses can be used with success in photographing the Spectralroth; however, the chrysoidine screens or other similar yellow dyes generally allow shorter exposures. For the extreme red, a combination of red copper and blue cobalt glasses can be used.

Congo, Benzopurpurin, Benzopurpurin 4B, Bordeaux extra, Orange R, Rouge Suisse,  $\alpha$ -Naphthol-Roth.

The dyes mentioned above are orange-red to violet-red, dissolve in water, do not decompose with ammonia and are good sensitizers of the bromide silver for green and yellow. They show a broad absorption band in blue to green, which is not sharply delimited towards the red end

but the absorption strip gradually moves as the concentration of the dye solution increases Drawn from Dr. Schumann's hand in Görlitz.

?) I dry the records free-standing in a completely dark, ventilated room, which takes 5-8 hours. One should use a sensitive type of gelatin dry plates from the trade (18° of the Warnerke sensitometer) for this experiment.

On the action of various dyes, etc. Al

further and further towards orange, while at low concentration it ends in green. The light sensitivity of bromide silver in the solar spectrum is increased by these dyes by a broad band in green to yellow or orange (E to over D). The sensitization closely follows the normal spectrum image on bromide silver; a sharply pronounced maximum cannot be observed with a small amount of dye added, but the effect of the light is from E to D (or with benzopurpurine 4B, Congo and the more deep red colors sometimes to over C). If more dye is added, the effect in the yellow-green is separated from that in the blue part of the spectrum by a point of weaker sensitivity, or the sensitivity to the rays from E to D is increased to a greater degree than to rays from E to F (see Curve 4; the dotted curve shows the course of the spectrum image with longer exposure).

The dyes are best used as baths with added ammonia for silver bromide gelatine. Of the dyes mentioned worked particularly well in my experiments: Benzopurpurin 4B, Congo, Benzopurpurin, then Orange R, Orseiline, Bordeaux extra, Rouge Suisse, -Naphtol red.

The colorants Congo, Benzopurpurin, Benzopurpurin 43 and Bordeaux extra are very similar in terms of their chemical composition. The last three dyes mentioned come from the paint factories formerly F. Bayer in Elberfeld and, according to the friendly reports of the gentlemen, have them

König, Böttger and Matthis, to whom I owe these dyes, the following composition:

o) NH, CH, 2 NH, CH, -N = N - C, H, CH -N = N C H 50.0Na \ S0.0.Na | C, H, -N = N C, H, 5S0.0Na CH, -N = N (C, H, 50.0.Na Na) NH, Sc, Na) NH, Congo Benzopurpurin 4, cH / DNH, yBOH -N = N C. H, 50.0Na CH, -N = N - C, H, -  
> 0.0Na

Ben zo purp. around

CH, -N = N C, H, S0.0Na N) OH

Bordeaux extra

er / a) OH / OCH, yH | CE NN ee soon. er N N, 0022 CH, -N = N C H, S0,0Na

Gas 2 et DoSCH, N 2) OH ar NOH

Azo blue benzeazurine)

1!) I reserve the right to publish my relevant investigations at a later date.

2) 4 cm? Dye solution (1: 400), 100 cm? Water and 1 cm? Ammonia.

3) 2 cm? Dye solution (1: 400), 100 cm? Water and! / , Cm? Ammonia.

#) I owe this dye to the kindness of Herr Dr. Schultz in Berlin. Congo was the first dye with which benzidine was introduced into the chemical industry. Since then, this basic material, together with the homogeneous toluidine, has formed the basis of a whole range of valuable dyes, which are characterized by the fact that they fix themselves on cotton without stain and are fairly genuine.

5) From Mr. J. R. Geigy's aniline paint factory in Basel.

6) Commercial dyes from the aniline factory in Elberfeld (formerly Bayer). 6°

asked JeNlssBridkest,

So it is benzopurpurine 4B the homologue of the Congo; while the latter is obtained by the action of tetrazodiphenyl on  $\alpha$ -naphthylamine sulfonic acid, benzopurpurine is produced by the action of tetrazoditolyl on  $\beta$ -naphthylamine sulfonic acid. Isomer with benzopurpurin 4B is benzopurpurin, which is obtained from tetrazoditolyl and  $\beta$ -naphthylamine sulfonic acid. Among these, benzopurpurin 43 seems to me to be the most suitable sensitizer. The dye has a stronger blue tint than Congo and further sensitizes to orange (red). The "a-dye" has a somewhat stronger effect than the " $\beta$ -dye". | |

Bordeaux extra!) Looks weaker, also azo blue?); even weaker benzo-azurine%) (I got all the dyes from the factory in Elberfeld). The presence of the hydroxyl group instead of the amido group seems to reduce the sensitizing effect, just as this substitution also influences the absorption capacity.

The entry of methyl into the dye makes the shade more bluish; the sensitizing effect then extends further against Roth.

Of the two isomeric dyes, benzopurpurine, the one from  $\beta$ -naphthylamine sulfonic acid has a slightly better sensitizing effect than that from  $\alpha$ -acid. I have also observed that other azo dyes, which belong to the same homologous series, are better than the preparations made from  $\alpha$ -naphthol

Sensitize those from B-Naphthol:

Fig. 18. Namely, oranges (Gessyaungd

Gr pErER Acid Orange (Geigy). The former is made from diazobenzenesulfonic acid and " $\beta$ -naphthol" produces and sensitizes the bromine

silver between Z and D

(similar to zn =  $\hat{a}$  € " E .-

Congo, but weaker). The isomer

= =

| | Acid orange is made from diazo- 4. Spectrum image on bromide silver colored with congo, benzopurpurin, &  $\beta$ -naphthol- | benzenesulfonic acid with  $\beta$ -naphthol and

red etc.  $\hat{a}$  € "5. Colored on bromide silver with certain types of indulins. sensitizes noticeably less to green and yellow. The interesting observation about two isomeric dyes is that they behave significantly differently as sensitizers in the spectrograph, less because of qualitative than quantitative sensitization. An orange-red dye, which differs from the orange R in that the sulfo group is absent and which is made



from diazobenzene and  $\hat{A}$  «-naphtol (private communication from Mr. Br) ohe Walter), shows a clearband of sensitization between D and egg m

Solar spectrum. This dye has the formula:  $\text{GH}, \hat{A} \in \text{"N} = \text{N-}\hat{A} \in \text{" -C, H .. (OH) \&$

If you compare the formula (according to Dr. Joh. Walter) of Orange R and Acid-

Orange, sosurrendered:

$\text{SO, Na SO, Na GH}, \hat{A} \in \text{"-N} = \text{N-} \hat{A} \in \text{" .C H. (OH) GH}, \hat{A} \in \text{"-N} = \text{N- C, H, (OH)}\%$  Oramererr  
Acid-Orange(Parazosulfobenzol  $\hat{A} \in \text{"}\hat{A} \in \text{"}\infty$  -naphtol) (Parazosulfobenzol  $\hat{A} \in \text{"}\beta$ -naphtol)

!) Made from benzidine and B-naphthol monosulfonic acid. ?) Prepared from tetrazoditoly  
and «- naphthol sulfonic acid. ?) From tetrazodiphenol ether and "-naphthol sulfonic acid.  
>

About the effect of various dyes etc. 45

Let us also consider a dye which I will call # -Naphtolroth and which I will give to Dr. I owe Joh.  
Walter. Itis made from% -diazonaphthalene (by diazotizing # -naphtylamine) and

Combine with  $\hat{A}$  «-naphtol produced. Its formula is:

$\text{Ch}, \hat{A} \in \text{"N} = \text{N}\hat{A} \in \text{" C HR2: t0H) e} \hat{A} \in \text{"}\hat{Z}$ -Naphtolroth (oxyazonaphthalene).

This dye is therefore homologous to the above-mentioned dye from diazobenzene. It is more  
violet-red and sensitizes the bromide silver to green and yellow (with longer exposure to over  
C). This naphthalene dye sensitizes more against Roth than the benzene dye and the former  
also has a quantitatively better sensitizing effect than the latter. However, he points to congo or  
benzopurpurine

no special

benefits. Induline.

Various blue, gray-violet to black coloring bodies come on the market under the name "Indulin",  
which behave similarly in their use for coloring and in their general chemical behavior. They are  
partly "alcohol-soluble" and partly "water-soluble"; the latter are mostly sodium salts of  
sulphonic acids of the alcohol-soluble indulins, change very little with acids, and are also fairly  
resistant to alkalis; with ammonia the blue color usually becomes more red-violet. In the  
absorptiometer 'but these dyes can be distinguished') and the sensitizing effect of the same on  
bromosilver gelatine is characteristically different at the same concentrations, so that a  
classification of the indulins could also be based on this with the help of the spectrograph, if the  
clear form of the maximum effects would not fluctuate with changing concentration.

The alcohol-soluble indulins do not tolerate ammonia. I use them as a bath for the silver-  
bromide plates, dissolving 1 part of dye in 400 parts of alcohol, and 5 of them

100 cm? Add water. In the same concentration I put the purely aqueous solutions of

the water!2-em 'too

soluble indulins and add 1 /, Å ° /, ammonia to the dye bath.

E IndalÄ ± n, which has no clear Sensibihisterunesmäaximum on bromosyllable: causes. This is where a water-soluble indulin belongs, which I received from Dr. Schuchardt from Görlitz and, according to the information from the factory where it was presented, was produced by melting amidazobenzene with aniline and sulfonating the product obtained. Mixing with rosaniline blue often gives the blue-gray color of this indulin for the trade more blued.

This dye suppresses the total sensitivity of the bromide silver to white light. With sufficient exposure in the spectrograph, however, a slightly increased sensitivity for the rays from E to AÄ ° appears in addition to the normal spectrum image. Behind a chrysoidine screen, the Fraunhofer lines emerge very sharply in the spectrum photography. I used the dye as a bath in the concentration 1: 4000 to 1: 10000. Adding ammonia is beneficial.

> bleu Couprer Ä¼md-ahnirche commercial grades of indulin, which are manufactured according to the denetrobenzene process; with a clear sensitization maximum in my opinion oramÄ ± oe.

!) The differentiation of the indulins according to their absorption spectrum is, according to my investigations, a striking one. As soon as my observations become numerous enough to base general conclusions on, I will follow up with more specifics.

2) The effect of the sensitizer decreases towards the red end of the spectrum. At times I observed abarely noticeable, very indistinct maximum of sensitization in the green.

46 32 M-Brothers:

Bleu Coupier is an indulin (nigrosine, violaniline), which is produced by heating nitrobenzene and hydrochloric aniline (with the addition of some iron, chlorine iron or chlorine tin).

As early as 1884 I described the effect of this dye with the following words: "Bleu Coupier causes a sensitization for the less refractive rays, which is remarkable because two maxima are asserted: one ingreen, the other in orange D! /, CÄ »)).

If this dye is used as an aqueous bath (2â € "6 cm? Of a solution 1: 400 to 100 cm<sup>3</sup> of water plus 1 /, â € " 1Ä ° /, Ä „tzammoniak), the maximum occurs in the orange stÄ (The middle of the maximum on the photographic Spectrum mbilde is at X â € " = 623 u wavelength). However, a weak sensitizing effect is noticeable for all the less refractive rays up to above A, which is particularly evident when using yellow screens (for example chrysoid solution); the part from D to C (or B) is particularly pronounced, on the other hand the effect is weaker in the outer red (curve 3 shows the effect of this dye with shorter and longer exposure). Of course, other commercial grades of indulin produced by the "nitrobenzene process" behave in the same way in the spectrograph. The characteristic maximum always occurs between C and D?).

I owe another type of violaniline to the kindness of Dr. Kalle in Bieberich. The preparation was made by the action of nitrobenzene, aniline, hydrochloric aniline and iron or tin chloride. The resulting alcohol nigrosine was sulfonated and, depending on the desired bluish shade, blued with waste aniline blue (which remains dissolved in the excess hydrochloric acid aniline during blue production, is precipitated

with plenty of water and sulfonated); in this case there is a mixture of dyes. Incidentally, the description of the sensitizing effect of this dye is anticipated by my earlier description of the Bleu Coupier.

Nigrosine (soluble in water) from the aniline dye factory of the "Société & anonyme des matières colorantes" in Paris (depot at W. Neuber in Vienna) behaves similarly to the dyes described.

5. Indulin  $\pm$  nzaus- nitrophenol and hydrochloric acid tr aniline by -Dr, Joh, Walter, is a dye which is soluble in alcohol and which is used as a bath of 10-12 cm? the alcohol solution (1: 400) and 100 cm<sup>3</sup> water was applied. This dye reduces the overall sensitivity of the bromide silver, but gives a weak effect from green to the most extreme red if the exposure is long enough. With this variety, however, one notices a slight increase in this sensitizing effect towards the red end (a<sup>o</sup> "A), while the indulin variety described in sub 1 gives silver bromide a sensitivity that decreases towards the red end.

4. Real blue from the aniline paint factory of Meister, Lucius and Bräunling in Höchst a. M. also belongs to the indulins (after a friendly communication from the management of the factory mentioned). It is "water-soluble" and "spiritus-soluble" on the market, in two different shades each (real blue R and 3R). The water-soluble real blue contains the sulfonic acid salts of the dye, they do not decompose with ammonia, but just turn red-violet. The alcohol-soluble varieties soon become cloudy with ammonia and excrete flakes. The aqueous-ammoniacal solutions of real blue sensitize for green to yellow. The broad (not always clear) maximum of the sensitization lies between E and D. A weak effect extends (becoming weaker and weaker) into the red.

The situation is similar with "water-soluble induline B" from the French aniline dye factory of the "Dociété anonyme" (obtained from W. Neuber, Vienna). In addition to the sensitization in green, this results in a weaker, indistinct maximum in orange (D! /, C) (curve 5). The clear maximum in orange, which characterizes Bleu Coupier, is missing in these indulin varieties. The "Induline B"

seems, however, to be the transition between "real blue" and "bleu coupier", so to speak.

!) Comp. pag. 1 of these treatises. ?) With ample exposure, the maximum spreads and blurs with the maximum in green.

About the effect of various dyes etc.

ATBile.

The bile, which is obtained by heating phthalic anhydride and pyrogallol and comes on the market as a violet dye, is a good sensitizer for green and yellow (to orange). You can dissolve it in hot alcohol (1: 1000) and then add 2<sup>o</sup> "10 cm<sup>3</sup> add to this solution, along with some ammonia. The violet-red solution, which is very unstable, is used for bathing bromide-silver gelatine plates. Even with a short exposure these show a strong maximum of the sensitization between E and D and with longer exposure the effect extends weaker to C (see curve 4).

With carbonate of ammonia, sodium bicarbonate, etc., the bile solution becomes more cherry red, tinged better, can be used in a more dilute manner and is not dissimilar to the previous solution; however, the maximum in green is narrower and weaker than when using the ammoniacal

Solution. Unfortunately, the alkaline bile supplements are inconsistent. Different green colors.

Some green colors, which are not on the market and which were given to me by Dr. Joh. Walter were kindly made available, sensitized the bromide silver for Roth. The "green from toluene aldehyde and dimethylaniline" (Concentration 1: 13000 together with some ammonia) there was a strong, narrow sensitization maximum at C to B at 30-150 seconds of exposure. "Green from methyl salicylaldehyde and dimethylaniline" behaved similarly. "Green from benzaldehyde and methylamylaniline", which was very detrimental to the overall sensitivity, expressed a very weak effect, as did "green from methyldiphenylamine and benzene trichloride". 2 I do not see any advantages in the use of these dyes as sensitizers

would be recommended.

Various orange-red and orange-yellow dyes.

Of the large number of orange-colored pigments which I examined spectrographically for their sensitizing power, a large part had a weak but at least recognizable effect on increasing the photographic sensitivity of the bromide-silver gelatine to green. Often only a moderate lengthening of the photographic spectrum towards green could be seen, sometimes a more or less clear maximum of the sensitization between E and D occurred.

I am content to simply enumerate the weak green sensitizers: Binitrofluorescein, Kettanatroilworeseein,  $\alpha$ -Chlornaphthal $\pm$ nsaures, - Nitrobenzultiuorescein). Monobromofluorescein is much worse than tetrabromofluorescein (i.e. eosin).

Various orange-yellow or orange-red dyes, when added to the bromosilver gelatin, showed little effect, for example: toluidine sulfonic acid diazotized with  $\beta$ -naphthol, the same with o-naphthol, sulfanilic acid with  $\alpha$ -naphthylamine; furthermore chrysoidins from: m-phenylenediamine + o-toluidine, m- amidobenzoic acid diazotized + resorcinol, m-tolylenediamine + o-toluidine. The orange made from diazoparanitrobenzene and resorcinol, which produced a weak sensitization maximum between E! / D, but without the eosin colors exhibiting any sensitizing effect, behaved somewhat better.

how to achieve.

$\Delta \pm$ ) According to Fehling's "New Handwording Book of Chemistry", Vol. IV, p. 635 illustrated. ?) Doesn't work better than benzylfluorescein (the commercial crysolin [Monnet]), but weaker.

48 J =

MeHrdeet

Diazaresorufin.

This red, beautifully fluorescing dye has a sensitizing effect on green, yellow and, if it is used for a longer period of time, even orange. This is what Dr. Mallmann and Scolik noticed while photographing color plates. The dye had not yet been examined spectrographically. I used it as a bath 1: 15000 to 1: 20000 with a small addition of ammonia. The silver bromide gelatine colored with it is sensitive from E to D ° / C; this clear band of sensitization usually reveals two maxima: one in green ( $\lambda = 560$ ), the other in orange  $\lambda = 614$ ). Longer exposure results in a weaker effect up to about 2. |

The similarity between the sensitization and the absorption of this dye, in which the latter also have two stripes in green and yellow, is noteworthy (cf. the table on p. 50).

It is also interesting that Bleu Coupier has a similar effect on silver bromide gelatine. On cursory inspection, the spectrum images on bromide silver, which is colored with diazo-resorufin, and those which are colored with Bleu Coupier, may under certain circumstances be very similar;

however, a more careful examination always succeeds in distinguishing them. Azo blue.

A wide variety of colors are marketed under the name of azo blue, and they are not the least bit similar in terms of presentation, composition and properties.

Azo blue from the paint factory in Elberfeld is a violet dye which is represented by the action of tetrazoditoyl on -naphthol sulfonic acid. With ammonia it becomes more reddish; but it also has a sensitizing effect without ammonia. This azo blue increases the sensitivity to green and yellow; with longer exposure the effect extends into the red.

Azo blue according to Nietzky has a similar effect on bromide silver! And does not seem to me to have any particular advantages as a sensitizer. Azo blue from the paint factory of Meister, Lucius and Brünning increases the relative sensitivity for green and yellow, less so for red.

It would take up too much space to account for the small differences in the behavior of the silver bromide gelatine, which is colored with the various azo blue varieties, in relation to the solar spectrum

as there is no particular theoretical or practical interest in this. Indophenol, anthracene blue, naphthol green.

These dyes are more or less weak sensitizers for the less refractive rays. Compared to Bleu Coupier and cyanine, indophenol works very poorly. Naphthol green (from the Gans' aniline paint factory in Frankfurt

a. M.) shows just as little as indophenol a strong one

Awareness. Anthracene blue (with ammonia) gives a slightly better effect in red.

About the Einwir

kung of potassium bromide on colored (sensitized) silver bromide.

It is well known that the presence of potassium bromide or another soluble bromide in photographic bromide silver layers the creation of the light image, but favors the purity and

1) About the representation of this dye, which is not on the market, see reports d. German. chem. Society,

17th year, p. 344.

About the effect of various dyes etc. Ag

Clarity of the image at the expense of photosensitivity. Pure silver bromide gelatine (without added coloring) is particularly damaged in its sensitivity to those light rays to which it is in and of itself less sensitive to light, that is to the less breakable rays (green, yellow, red) and the external ultraviolet rays ;

the spectrum image therefore appears shortened on both sides and the maximum effects emerge particularly clearly.

Bromine-silver, which is sensitized with dyes, behaves in a very similar way. If a small amount of potassium bromide is added to the dye baths (eosin, erythrosine, cyanine etc.), the silver bromide plates are bathed and then checked for their color sensitivity in the spectrograph, one notices that the sensitizing photographic effect has been reduced. The areas with the weakest effect are always damaged first, for example the minimum effect on cyanine plates at E in green, which combines the maximum effects in blue and orange, is suppressed first. As a result, the sensitization maxima are resolved into narrower, stronger stripes, which emerge more precisely. Already 1 to 2 drops of potassium bromide solution per 100 cm<sup>2</sup> of the dye bath in which the silver bromide gelatin plates are bathed exert a noticeable influence; such a small addition can sometimes be of advantage in the case of obscure plates. However, where the most complete possible reproduction of even very weak light effects is concerned, no potassium bromide should be added.

It should also be mentioned that the potassium bromide always makes the reduction of the silver bromide more difficult, both the reduction by the light and by the developer; therefore it also acts retarding when it is added to the pyrogallus developer or iron oxalate developer. This addition is advantageous when photographing very intense light sources.

About the connection between the absorption of dyes and their photographic sensitizing effect.

In an earlier essay!) I had discussed the connection between the absorption of dyes and the maximum sensitization to silver bromide, the wavelength of the light rays most strongly absorbed in colored gelatine sheets and, on the other hand, the wavelength of the strongest in the region of the sensitization indicated photographically effective rays and the shift of the sensitization maximum against Roth to be determined with thunic accuracy.

I also investigated a few other dyes, which caused pronounced sensitization maxima on bromide silver gelatin, in the same direction. In Bleu Coupier and Diazoresorufin in particular, which show two absorption bands, two more or less clear sensitization bands can be found in the spectrum image on the silver bromide gelatine dyed with it, and each of them is based on the one already mentioned in the earlier treatise pag. 20 and 35) shifted towards the less frangible end of the spectrum.

So these results show that the dyes mentioned sensitize the bromine silver to the less breakable rays according to the same proportions as those I examined in previous years. The shift in the sensitization maxima, which correspond to the absorption, is also within the same limits as I stated at the time.

In both Bleu Coupier and Diazoresorufin, two more or less distinct maxima are noticed in orange and green, followed by a weaker effect down to red. Since one of the pigments that act in this way is fiery red, the other indefinitely blue-violet 15% so. is. This is a great proof for the claim (incidentally not contested by anyone) that the physiological intrinsic color of a body has nothing in common with the sensitization phenomena in the spectrum. In

1!) Comp. p. 26 of these treatises.

=.

50 M J. M. Eder.

In this case, the connection between the sensitization and the absorption emerges again clearly, in that the two dyes mentioned have two absorption bands and accordingly give two sensitization maxima. In any case, the shift in sensitization to the less breakable end of the spectrum occurs and Bleu Coupier, whose absorption strip is farther from orange than the corresponding one of diazoresorufin, also causes the position of the sensitization.

Applied dyes

|

Middle of the maximum of the absorption of the color in colored gelatine foils

Center of the maximum of photographic sensitization on dyed

Difference between the absorption maximum in the gelatine and the sensitization

Bleu Coupier

Diazoresorufin

n

Green from methyl salicylaldehyde and dimethyl anil

± lin Orseiline

there are two absorption bands:

1. a strong one in orange-  $\lambda = 986$  and

2. a weaker one in the green

there are two absorption  
bands:

1. one in orange-yellow at  $\lambda = 544$

2. one in green at  $\lambda = 544$

gives an absorption band in Roth at  $\lambda = 10633$

Silver bromide gelatine maximums of the colored bromide silver in millionths of a millimeter  
wavelength there are two awareness-raising development cooperation bands:

1. one in orange red at  $\lambda = 1023$  nm

2. a weaker broad band of awareness in

green there are two awareness-raising

bands: do leinessim- Orange at  $\lambda = 614$

and

2, one in green at  $\lambda = 560$

gives a sensitization OR band in Roth at  $\lambda = 660$

gives a broad awareness-  $\lambda = 23$  to

33

gives a broad, strong absorption band in green and yellow-green; then weak absorption up  
to Roth;  $\lambda = 580$  to  $590$

rungsband, strong from gran. to yellow 'borders against red about as

(? unsure)

against orange. With this, the sensitization spectra of both dyes can be differentiated upon  
careful examination and furthermore with the stronger sensitization that Bleu Coupier  
generates for the red rays from  $\lambda = 600$  to  $\lambda = 650$  nm.

There is another analogy between the sensitizing strips and the absorbing strips. In both cases,  
the width and course of the curve, which expresses the effect in question, changes with the  
concentration.



Most of the sensitization streaks of the dyes on silver bromide occur at very significant Dilution (for example under Y / non) as weak shadows. As the concentration increases,

About the effect of different dyes etc. 51

the sensitization stripes are stronger and as a rule rise to a more or less clear maximum, which has a constant position in the spectrum. With an even higher concentration, the excess amounts of dye have a detrimental effect on the overall quantitative sensitivity of the colored bromide silver, and with a significant dye content it can even (as Be Ne oge | first showed and I can fully confirm) the sensitivity side effects occur, certain spectral regions are suppressed and the effect of the dye addition comes close to that of a colored screen and is made even worse by the harmful influence that most colors (as well as numerous other salts) have on the light sensitivity of the bromide silver As soon as their quantity exceeds a certain limit, so that the awareness bands can even become narrower again. |

The concentration limit within which the dyes have the most favorable sensitizing effect is variable depending on the nature and tinging power of the dyes. In the case of eosin, the effect is best at high dilution (approx. 1: 30000 to 1: 50000); The strongly stimulating benzopurpurin and congo must also be used in diluted form. The indulins and cerulins can be used much more strongly without harm and the best effect is achieved even with a concentration that is several times stronger. |

For each dye, the best concentration of the sensitizing baths has to be determined experimentally. be averaged.

Behavior of silver bromide gelatine (without added coloring) against the solar spectrum.

It is known that silver bromide gelatine is extremely light-sensitive for ultraviolet, violet and blue, but that the light-sensitivity decreases very sharply from blue-green to yellow and red. As a rule, the solar spectrum cannot be clearly photographed via the Fraunhofer line C on ordinary (not mixed with dyes) silver bromide gelatine plates. Because of the multiple reflections from the prismatic surfaces (in my apparatus, three prisms), such masses of diffuse light get into the apparatus that, with longer exposure, an even blackening of the entire image area is obtained. So you can not expose until the orange and red have had a strong enough effect, since the diffuse white (and the very effective blue) light used to cause total decomposition. If, however, the main masses of blue and violet rays are excluded by placing yellow or red glasses in front of the slit of the spectral apparatus, good photographic spectrum images are obtained which extend into the red; yes, Draper could even photograph the infrared behind red glasses on silver bromide gelatine, which contained no dye as a sensitizer.

leh hand chrysoid screens as see r well suited to suppress the blue. An alcoholic (or aqueous) solution, 1: 10000 to 16000 in a tub of 11 mm (immediately in front of the column), suppresses the rays from F to G; in greater concentration even from E to almost F #. From Ean the light passes through, slightly weakened, to the extreme red; likewise the ultraviolet is only weakly attenuated. |

The sensitivity of the bromide-silver gelatine to light can easily be followed up to the red behind yellowscreens. The plates sensitized with suitable dyes are, however, less sensitive to light

the less refractive rays far superior to ordinary plates. 1

Spectrographic investigation of normal light sources and the usefulness of the latter for photochemical measurements of light sensitivity.

J. M. Eder.

(Presented at the meeting of the Imperial Academy of Sciences on April 23, 1885.)

For the photometry of the optical brightness of different light sources, Hefner-Altenek and after him Siemens proposed a flame of amyl acetate with a flame height of 40 mm and a cotton wick with a diameter of 8 mm!), Which gives a very regular and constant light. Abney<sup>°</sup>) and V. Schumann<sup>€™</sup>) also recommend this light source for determining the photographic sensitivity of various preparations, that is for "sensitometry".

In order to investigate the usefulness of amyl acetate, which is burning in a lamp, for photochemical purposes, I photographed the spectrum of it in my large Steinheil glass

Spectrograph and compared the W102:

H 6 the individual parts of this spec-

N M L K

trums with that of sunlight and other normal light sources,  
which are used in photography,

I H

DE || namely the candlelight, the blue

phosphorescent calcium sulfur

1. Spectrum of sunlight, photographed on silver bromide gelatin. â€" and the magnesium light. 2. Spectrum of burning amyl acetate, photo- on bromide silver gelatin

graphed. â€" 3. Spectrum of the blue phosphorescent calcium sulfur. The photographic recordings

| show the re-

results when the intensity of the effect in the blue is equally strong. No. 1 in Fig. 19 shows the image of the

Sun spectrums on silver bromide gelatine, which has the maximum effect in my spectrograph at G', F has. The effect is still strong, but gradually decreasing, far beyond the visible violet into the ultraviolet against M.

No. 2 presents the spectrum picture of the burning amyl acetate. This does not extend that far into the ultraviolet, even in the visible violet (G to F7) it is very weak. The maximum of the

1) Elektrotechnische Zeitschrift, Vol. V, pag. 20.?) Photographic News, 1884, pag. 787.?) Photographisches Wochenblatt, 1885, pag. 34.

Spectrographic examination of normal light sources etc. 33 \

Effect is further against light blue, much closer to F than in the previous F all. With longer exposure, the intensity of the spectrum image of amyl acetate increases significantly in intensity at F and further against green, but the effect in violet and ultraviolet always remains relatively very weak, which agrees with Schumann's statements.

This shows that the burning amyl acetate is relatively poor in violet and ultraviolet rays (in comparison with sunlight) and that the relative brightness predominates in the blue. The brightness in green, yellow and red is also very strong; However, these colors have only a small effect on uncolored bromide silver and therefore the effect is missing here, which is very clearly visible with colored bromide silver?).

The photograph of the spectrum of an ordinary glowing gas flame is very much like that of amyl acetate; however, it shows a somewhat greater relative brightness in the violet.

These results confirm the investigations by Crowa)), Bickeriweo)) and Å ±., Which optical brightness of the luminous part of the flame spectra had been investigated by means of quantitative spectral analysis, which I have already reported in detail in another placeÂ®).

There is also the blue phosphorescent light from sulfur calcium ("Balmain's luminous color"), which Warnerke proposed as normal light and which has since been used in practice for determining the sensitivity of photographic plates using "Warnerke's Sensitometer"?). No. 3 in Fig. 19 shows the full visible spectrum of phosphorescent calcium sulfur. It is limited to a narrow band between G and F in blue, which disappears against purple and green. Abney®), who had also examined this spectrum, noticed a second, much weaker band from E to C; however, V. Schumann), who occupied himself with the same subject, could, as little as I myself, could show yellow or red

in the g notice the named phosphorescence spectrum.

The question now arises: Are the sensitivity ratios of several light-sensitive specimens constant as soon as they are determined with different light sources?

There are isolated reports about this: AbneyÂ °) found that silver bromide gelatine plates appear much more sensitive to blue phosphorescence light in Warnerke's sensitometer than wet iodobromo collodion plates, while the difference is not as great in daylight or gas light. Pickerin gâ €) examined 15 different commercial "bromide silver gelatine plates" which contained either pure bromine silver or bromide silver in addition to iodized silver and chlorine silver. The ratio of light sensitivity varied

significantly depending on the light source used. For example, some plates that were equally sensitive to gas light showed a 2–30 fold difference in sensitivity to daylight. I extended my photometric experiments to include silver bromide, silver iodobromide, silver chloro gelatine emulsion, wet iodobromo collodion and colored (eosin-containing) silver bromide gelatine emulsion and used daylight, gas light, Hefner-Altenekâ €<sup>TM</sup> s amyl acetate light, Wearnerkeâ €<sup>TM</sup> s blue phosphorus

escenz normal light and magnesium light into my investigations.

1) cf. pag. 1 of these treatises.

2) Supplement to the Annal. d. Physics and Chemistry, Vol. II,  
p. 655.S-1bid.,. Vol. IV, pas. 728:

4) Eder's "Detailed Handbook of Photography", 1884, I. Theil, p. 102.

5) Eder's "Detailed Handbook of Photography", 1884, I. Theil, p. 201 and IH. Theil, Issue 9.

6) Photographic News, 1882, p. 230.

7) Photographisches Wochenblatt, 1885, p. 39.

8) Photographic News, 1882, p. 230. See also Eder's "Detailed Handbook of Photography", 1885, Part II,

p. 42. 9) Photographic Journ., 1885,

p. 71.54 J. M. Eder.

"The results are clearly arranged in the following table. In this table, the ratio of the light sensitivity of a pure silver bromide gelatine plate to the light sensitivity of various iodine-bromide silver, chlorine-silver and eosin-bromide silver layers is given, and the sensitivity of the bromine-silver to daylight is assumed as a unit Are in all cases outstanding

call images meant, namely alkaline developers for gelatine emulsions, and wet iodine brominecollodion but acidic iron vitriol developer as they are used in practice.

The relation for di photosensitivity to photosensitivity as E ee> von De nassem Jodbromcollodion. . . as daylight EN j blue> R Fa 0 | Phosphorescent light r N KR: I amyl acetate light chlorosilver melee he 22, 2 I pe daylight 5 bear eabiser. Amyl acetate light R Re N newly magnesium light bromide silver eosin- containing bromide silver gelatin. klsnbisee., | Daylight gelatine a l IW @ B1is = s amyl acetate light x Å £ 1:10 to 60 sodium light?) Be (blue? Ra: | phosphorescent light iodobromide silver gelatine (ie finished | bromide silver gelatine with 10 to \ er - daylight 20Å ° /, iodized silver gelatine mixed) | 5 | aues - Et; | ii Å¼ Ey \ Phosphorescent light

It follows clearly that the ratio of the sensitivity of different light-sensitive substances fluctuates very significantly, depending on the quality of the light source. These fluctuations are so significant that they can amount to 100 times that of the uncolored bromine silver and the eosin-containing bromine silver, depending on whether they are tested in daylight or yellow sodium light. In the case of bromo- and chlorosilver gelatine, for example, the ratio of the sensitivity of both fluctuates by 10 times, and in the case of silver-bromide and silver iodobromide gelatine by 2–4 times, depending on whether one is exposed to daylight or amyl acetate light (or what is approximately the same, gas - or candlelight) carries out the sensitometric comparison. |

The key to this phenomenon naturally lies in the different color sensitivity of the individual photographic preparations; for example, silver gelatine has the maximum sensitivity to light for the borderline between the visible and ultraviolet, silver gelatine for light blue (see pag. â € and 10 of these treatises); wet iodobromo collodion lies between the two. If the spectra of the various light sources show a different brightness in the various colored parts of their spectrum, then there must be considerable fluctuations in the relation of the light sensitivity.

') A non-luminous gas flame into which sodium chloride has been

introduced. Spectrographic examination of normal light sources etc. 55

It also follows that neither the sensitometric determinations for gas or amyl acetate light nor those for blue phosphorescence or magnesium light also apply to daylight. In some cases the results of the amyl acetate light are closer to daylight than the phosphorescent simple, but not in other cases; If, on the other hand, one works with one and the same silver compound (for example bromide silver) in different molecular states with different degrees of light sensitivityâ €), the results are not so different. If the sensitivity of a digestion "ripened" bromosilver gelatin was twice as sensitive when tested in Warnerke's sensitometer (phosphorus escape light) than before "ripening", I found roughly the same result in daylight. In such cases, Warnerke's sensitometer or other such instruments will still be recommended if the numbers are not absolutely accurate.

1) For example, silver-bromine gelatine, which is made more and more sensitive to light through prolonged digestion (so-called "ripening").

Photometric experiments on the sensitizing effect of dyes on silver chloride and silver bromide with different light sources.

Of

J. M. Eder.

(Presented at the session of the Imperial Academy of Sciences on December 17, 1885.)

In a previous paper!) I have shown by a number of photometric measurements that the ratio of the light sensitivity of different substances fluctuates very significantly, depending on the quality of the light source. At that time I determined in particular the fluctuations in the relative light sensitivity of silver bromine gelatine, silver chloride gelatine and iodobromo collodion to daylight, lamp light, magnesium light and phosphorescent light.

Later I tried to determine to what extent the relative photosensitivity of bromosilver and chlorosilver gelatins to different light sources is influenced after they have been sensitized by different dyes; Since these results serve to characterize the light source as well as the light-sensitive substance, I established these relationships numerically.

I used chlorosilver gelatine?) With iron oxalate or iron citrate development 9), "Iern bromosilver gelatine with alkaline pyrogallol developer; both were bathed with different dye solutions (approx. 1: 20,000) and thereby sensitized to the less breakable rays. Daylight and gas light (argand burner) served as the light source. The photometric measurements became

Warnerke's Sensitometer \*) used. The relative photosensitivity of the preparations was as follows: With gas light (10 minutes exposure):

Light sensitivity of common silver chloride gelatin | N  $\hat{=}$   $\infty$  Chlorosilver gelatine- + 0:02  $\hat{=}$   $\infty$  /, eosin. =  $\frac{1}{2.008}$ , -Bos  $\hat{=}$   $\frac{1}{5}$   $\hat{=}$   $\frac{1}{120.02}$ . vOyanman, ar. Beer

!) Comp. p. 52 of these treatises.

?) Comp. Eder and Pizzighelli: "Photochemistry of Chlorine Silver", sessionber. d. kais. acad. d. Science in Vienna, January issue 1881, in which the photographic process invented by the authors is briefly described.  $\hat{=}$   $\infty$  "For more detailed information, see Eder  $\hat{=}$   $\infty$  s" Detailed Handbook of Photography ", 1885, III. Part.

%) This is a mixture of potassium oxalate or ammonium citrate with iron vitriol solution.

4) For a description of this instrument see Eder's "Detailed Handbook of Photography", 1885, III. Part. - The blue phosphorescent panel of the sensitometer was removed during these experiments and the instrument was held against the gas light.

Photosensitivity of silver bromide gelatine 50 ± 0.032 /, eosin. ± 2400-18 1120: x | - 20:02, Cyan ± n - 45 to 55 Ber Fageslicht: light sensitivity of ordinary chlorosilver gelatine =. le) ± 0.06 ± 0.06. ± 0.02%, Bosnz 08 ± 0.06 R 752.008, Bosn = ± 0.06koubisel h 5 e 20: 02 ± €, = @ yan ± n ± 20: 3 to 0: 5 ± » ± 0.06Bromosilver gelatine ee ee Na en; : i 0030 SEO me a eipies r 5 R 10:020a ee er De bisle

The chlorosilver gelatine mixed with dyes gives much more intense photographic images than the uncolored if there is sufficient light; furthermore, are the photos on the former free of halos or irradiation phenomena?). At. This beneficial effect of the dyes is even more evident than with silverbromide platesâ€™ (TM).

As a new factor, we also have the addition of dyes to the chlorine silver prior to production: the image closed. to mention. These, color. the "reduced silver" of the photograph remains different than is the case with pure chlorine silver; the new color will persist even after every trace of the color has been washed out by the developing, fixing and washing baths. For example, while my chlorosilver gelatine in the iron citrate developer gave an olive-brown appearance, the eosin-chlorosilver takes on a black to reddish-brown color and cyanine-chlorosilver also gives darker shades \*).

This phenomenon is explained by the different color sensitivity of the preparations and on the other hand through the uneven distribution of the colored rays of light in the various lightsources.

?) A monograph on photographic irradiation and lateral extension of the light image is contained in Eder's "Detailed Handbook of Photography", 1884, Part II, p. 55.

Â®) Such colorations should be of noteworthy use in photography of very bright objects, for example the sun. Not only eosin and cyanin have this property, but also many other dyes; in this connection it does

not seem necessary that the dye should be a sensitizer for the silver chloride for the less refractive rays, although in my experiments the effect was most striking in the latter case.

\*) For example, especially if there is a lot of ammonia or ammonium carbonate in the bath in addition to the dye, as soon as the gelatin emulsion is sensitized in it or the dye of the ammoniacal emulsion during the presentation

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That the photographic copying processes with gelatine emulsion, in particular with chlorosilver gelatine when using lamp light, benefit from these observations, does not need any further

Executions.

Notes on orthochromatic photography.

The spectrum of the petroleum flame and the gas light shows, in comparison with the spectrum of the diffuse daylight and sunlight, a significantly greater relative brightness of the less breakable rays. With the same overall brightness of the spectra, the brightness in the yellow is pretty much the same in both cases; in orange the petroleum spectrum is 7 times brighter than the solar spectrum, in contrast 2 times less in green, in blue 40 times less than the latter (Vierordt).

Therefore, photographic preparations which are naturally sensitive to red and yellow must decompose relatively more quickly in petroleum or gas light than those which are particularly sensitive in blue and violet; I first proved this in my paper (May 1885) cited at the beginning with eosin bromine silver, which was found to be  $S$  times more sensitive to lamplight than uncolored bromine silver, while in daylight the sensitivity of both was about the same. This also explains the low light sensitivity of the chlorosilver gelatine, which has the maximum sensitivity at the border between violet and ultraviolet, to petroleum light. This also explains the significantly increased overall sensitivity of the same preparation to petroleum light after the addition of eosin, which increases the sensitivity to yellow-green, and of cyanine, which makes red-sensitive.

The above considerations also explain some of the observations made in "orthochromatic photography". Namely, the recording of colored objects (paintings, etc.) is carried out in the same way that a yellow disc is attached in front of the photographic objective in order to dampen the blue and violet while in an "orthochromatic plate" is exposed in the photographic camera. This is taken to mean plates whose sensitivity to yellow and orange has been increased by adding dyes according to Vogel's principle of sensitizers.

In spite of the fact that the effect of the sensitizers is very noticeable and does not escape observation with some attention, neither in spectrographic nor in practical photographic work, it has nonetheless been claimed that the yellow glass is the main thing and that the sensitizer is superfluous.

This is not correct, because the yellow glass only mutes the blue and purple of the painting; but the photographic plate is not sufficiently sensitive to yellow etc., it goes without saying that the yellow pigments cannot have any photographic effect on the plate.



However, no pigment reflects a pure spectral color and some red pigments reflect blue light; some yellow pigments reflect blue and green (for example picric yellow, some types of aniline yellow). Then, because of their green and blue content, such pigments will act on an ordinary photographic plate and on superficial observation one could speak of a photographic effect of the "yellow". With ordinary silver- bromine gelatine, but better still with silver-iodine-bromide gelatine, and using a yellow disk, useful photographs of paintings in which the blue and violet are muted; but if, for example, ultramarine is next to chrome yellow and chrome orange, these plates are no longer sufficient because the yellow is relatively too dark, while orthochromatic plates give a correct picture behind a light yellow plate.

Without the yellow disc, the orthochromatic silver bromide gelatine plates shown so far reproduce the optical color effect of a painting in daylight.

Some color mixes are not correct because the plates are relatively too sensitive to blue.

1) Observations by H. W. Vogel, Vierordt and others are available on the spectral composition of the light reflected by pigments, so I refer to these investigations here.

Photometric experiments on the sensitizing effect etc. 59

In the case of colored chlorine silver plates (as I published a year ago) or wet eosin bromine salt Collodion (Vogel), the yellow disk is superfluous because the sensitivity to blue is less than the sensitivity to yellow. The yellow disk can also be dispensed with if the paintings etc. are illuminated with yellowish light. You color the electric light yellow or use the more yellow gas or lamp light. The latter was first demonstrated by Schumann (November: 1885) with silver bromide plates, which were colored with cyanine, then Vogel with azaline plates; but the same applies to plates which are colored with eosin or erythrosin etc.

I then made a series of experiments and photographed the spectrum of lamp and sunlight on different types of plates.

Curve 1 shows the photograph on eosin-bromide-silver gelatin (lamplight). Curve 2. The same (sunlight). Curve 3. Cyanine-bromide-silver gelatin (lamp light). Curve 4. The same (sunlight). Curve 5. Different types of iodobromide silver gelatine (lamp light). Curve 6. The same (sunlight).

You can see that with lamplight (petroleum and gas light) Fig. 20.

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the photographic yellow, respectively red effect in the spec! triumphphotographie outweighed the blue effect once the plates were sensitized with eosin or cyanin.

In the solar spectrum, however, the opposite is the case.

The same applies to other sensitizers whose sensi-

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bilizing effect on bromide silver I described in detail

and as curves drew. If one compares the effect of

the solar

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spectrums, which went through yellow glass, with the effect of the spectrum of gas or petroleum light on eosin plates and the like, the similarity between the two is striking.

Iodobromide silver gelatine, however, lags behind the bromide silver plates sensitized by dyes in terms of sensitivity to the less refractive rays, even with lamp light. Pigments which approximate pure yellow, orange or red can therefore (in comparison with light blue, for example ultramarine) on such plates not be reproduced with the same brightness as on orthochromatic plates; unless one tries to make do with very dark orange glass and a much longer exposure time in the former case and even then the effect is often insufficient.

If, with orthochromatic plates, paintings can be photographed in petroleum or gas light with approximately (!) The same final results as in daylight with certain yellow panes, the results of the spectrographic examination are confirmed by practical experience . It can be foreseen, however, that with the change in the color sensitivity of the preparations and

the permeability of the yellow disk for colored light, the two lighting methods

fluctuate rather:

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About some methods of photographing the spectrum in its various districts with sensitized silverbromide plates.

Of

J. M. Eder.

(Presented at the meeting of the Imperial Academy of Sciences on July 8, 1886.)

Photograph of the spectrum with consideration of the most fragile parts from green (Fraunhofer line F) to the extreme ultraviolet.

The usual bromosilver gelatine drying plates were excellently suited for the photography of the more breakable part of the spectrum because of their great sensitivity to light. Completely displaced because the sensitivity is 5 to 30 times greater and the exposure time can be extended to several hours, even several weeks!) without damage.

Since the usual silver-bromide gelatine plates have the maximum of their sensitivity in blue (see Fig. 1 on panel I) and reproduce this area, as well as the violet and ultraviolet on the one hand and the blue-green on the other hand, there are no other aids to the photography of these rays - medium required. It should be mentioned, however, that the commercially available drying plates do not all have the same high degree of light sensitivity and that comparative sensitivity tests should be carried out beforehand with the Warnerke's sensitometer?).

However, one can photograph the solar spectrum up to about C (and even further from Roth) on ordinary bromide-silver gelatine plates if one exposes for longer and if one brings colored screens in front of the slit to exclude the blue part (cf. the photography of the solar spectrum on ordinary silverbromide plates in Fig. 11, panel ID).

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) In order to be able to photograph the spectrum of the non-luminous flame of the Bunsen gas burner, I had to expose the blue flame cone for 12 hours to 2 days and I received the Swan spectrum with much more lines than clearly on erythrosine plates are given in the Lecoq de Boisbaudran's spectral tables.

The upper, colorless part is much fainter; up to now it has been assumed that it gives only a weak continuous spectrum (without lines) (Swan). After 8-14 days of exposure to light, however, I received a spectrum of this part, which partly shows the main lines of Swan's spectrum, but also an apparently continuous spectrum in blue to violet, which is traversed by numerous penumbra bands. |

?) In photographic practice, highly sensitive plates are required to be 20 to 23 ° Warnerke; Incidentally, plates of 24 to 25 ° Warnerke are currently being sold by some factories.

Photograph of the spectrum etc. ZR 61

However, the Fraunhofer lines of the solar spectrum in the less fragile part become noticeably sharper and more pronounced when the silver bromide is sensitized by suitable dyes. The silver bromide is not only much more sensitive to light for the relevant yellow, red etc. rays (for example erythrosine, cyanine, cerulein), but the spectrum image is also much sharper and better defined. This latter advantage should not be underestimated. Some dyes (for example certain indulins), which are added to the bromide silver, cause no gain, but sometimes even a loss of quantitative sensitivity (or overall sensitivity to white light); Nevertheless. Their use can be useful for coloring the bromide silver layer,

because with long exposure and intense light sources a better definition of the photographed spectra and clearer differentiation of the sharp lines is obtained than with ordinary (not

dye-containing) bromide silver is possible in the less breakable part.

Photograph of the spectrum with consideration of the less frangible part from green to the outermost red.

The epoch-making discovery of the effect of the dyes as sensitizers for the less refractive rays by H. W. Vogel provided the means to make the silver bromine sensitive to green, yellow and red using suitable dyes. It is well known that the dyes have an extremely different effect on bromide silver and they are. Lengthy investigations are necessary in order to ensure empirically the sensitizing effect of the individual dyes and their most advantageous application. I refer to my earlier papers<sup>62</sup>), Which deal with this subject and mention that V. Schumann in particular obtained excellent results with his erythrosine and cyanine plates in spectrophotography.

However, I am giving here a selected small number of sensitization methods for bromosilver gelatine, which gave me the best results from hundreds of experiments in photography of the solar spectrum (as well as in spark spectra and spectra from Geissler's tubes) to give the spectral analyst guiding points of view as to the appropriate spectrographic methods.

The commercially available orthochromatic plates are mostly colored with erythrosine and then show (as I first published in 1884) a maximum of sensitivity in green to over D. Erythrosine plates are not suitable for photography of the spectrum against Roth. The azalin plates (according to H. W. Vogel) that occur in the trade are not only sensitive to green and yellow, but also to red (up to over C); they are colored with a mixture of cyanine and quinoline red<sup>7</sup> (Mallmann and Scolik, H. W. Vogel).

Since we currently do not know of any colored silver bromide plates which reproduce all spectral regions photographically to the same degree, it seems more advantageous to sensitize the silver bromide with suitable dyes for each spectral region which one wishes to examine. I have given the dates for this in my earlier treatises, and in what follows I give my mode of operation, as I have worked out it in the following.

I use the following preparations to photograph the individual spectral regions:

From ultraviolet to blue-green (Fraunhofer line E): Ordinary silver bromide gelatine plates or better iodine bromine plates with  $3 \times 10^{-5}$  ° /, iodized silver (see Fig. 1 and 2, panels I and II).

1) For example, cerulein, sensitogreen, benzopurpurine and other dyes promote the sharpness of the Fraunhofer lines in the solar spectrum not only in the less breakable part, for which they act as sensitizers, but also in the ultraviolet.

2) cf. pag. 1, 26 and 41 of these

treatises.<sup>62</sup> | J. M. Eder.

From ultra violet to yellow (something about: D):

1. Erythrosine plates, which are almost equally sensitive to ultraviolet to blue, but have also become so sensitive to the dye in green and yellow (intense maximum between E to D) that there the effect is approximately the same as that in blue ( see Fig. 2, panel I). The erythrosine plates perform just as much in the blue to ultraviolet parts as ordinary plates, but are considerably superior to these in the green and yellow; thus the erythrosine platelets are decidedly preferable. |

2. Benzopurpurine 45 does not make the bromide silver as sensitive as erythrosine, but gives a broader band of sensitization, which is closer to the blue effect and works further through D into orange (see Fig. 4, panel I). Benzopurpurine plates cannot replace erythrosine plates in terms of sensitivity. But where there is nothing to do with an exposure time that is 5 times longer, the former are preferable because of the more even effect in green to orange.

Quinoline red (Vogel) also works well.

From ultraviolet to red (against C and above to B). In this district, cyanine plates do the best. They usually require a longer exposure than normal plates or erythrosine plates, but give the ultraviolet, violet to blue-green very clearly, show a place of insufficient sensitivity in the green (F1 /), E to E! /, D), are less sensitive to yellow than erythrosine plates, but show a high sensitivity to orange and red, also to yellow (see Fig. 7, Table I). With yellow or red umbrellas, the effect appears in yellow to red. especially clear demo (s2.749.0 ,. Vafel

Sensito green is also a good sensitizer for orange and red, which is similar in its effect to cyanine, but due to its lower sensitivity to red it only becomes fully effective with the use of yellow umbrellas (for the solar spectrum) (see Fig. 5, panel I).

Denzoranselarbisen = up to the red district of the sun spectrum up to the Ainikaroi), except for cyanine, is best obtained on cerulein plates with red glasses (D to A). The part from D to B is obtained with a considerably shorter exposure on cyanine or Sensito green plates; in terms of uniformity of action up to above A, however, cerulein is superior (see Fig. 10 and 13, FatelT)):

Colored screens in front of the slit of the spectral apparatus are very advantageous in the case of very bright light sources, which contain all different colored light rays (for example sunlight, electric light), in order to exclude those light rays which are not included in the investigation. It is always advisable to prevent extraneous light masses from entering the device.

With line spectra (for example hydrogen in Geissler's tube) this caution is superfluous. | |

As a yellow screen I use either yellow glass, which mainly absorbs ultraviolet, violet and blue, or chrysoidin solutions, which absorb blue in particular. Red glasses let through almost only the orange and red light from D to A.

Yellow chrysoid screens behave spectroscopically much differently than yellow glass. While yellow glass (so-called carbon or wood glass) shows a gradual absorption, which is strongest in ultraviolet and gradually decreases towards blue, chrysoidin shows in the middle of the spectrum an absorption tape (see Figures 11 and 13, panel II). This emerges very clearly from the comparative spectral photograph on Bleu Coupiér plates behind yellow glass and chrysoidine screens (see Fig. 8, panel II with yellow glass and Fig. 12, panel II with chrysoidine screens).

The absorption band of the alcoholic chrysoidin solution reaches its maximum between F and G in the solar spectrum. So it is the blue rays that are suppressed, which on bromine

silver gelatin exert the strongest photographic effect while violet and ultraviolet, as well

Photograph of the spectrum, etc. 63

on the other hand green, yellow and red penetrate through with little weakening!). I mostly use alcoholic chrysoidin solutions of 1 part chrysoidin in 10,000 to 16,000 parts alcohol. The layer is 11 mm thick and is located in a plane-parallel tub directly in front of the gap.

Behind such chrysoidine tubs, the photographic effect of the solar spectrum can be examined much better against green to red, because the violent blue light is excluded. Namely, the blue light, which is contained in the never missing scattered light?) In the spectrograph, has a damaging effect on the clarity of the weaker-looking spectral regions. However, if you exclude the main masses of blue and violet light, you get very pure spectrum images from green to red. Behind chrysoid screens you can even follow the light sensitivity of common bromosilver up to B, and even A. In particular, I kept the area from F to D in focus (with ample exposure) (see Fig. 11, panel II). |

Chrysoidine screens are therefore particularly recommended as soon as you are studying the ultraviolet against F and on the other hand from green (F to E), yellow and orange.

Yellow carbon glass absorbs ultraviolet, violet, blue and a little green in particular, with the absorption gradually decreasing from the more breakable end towards the less breakable end (°).

Such screens can only be used if the visible spectrum is from H to yellow. 5

The blue end of the spectrum is attenuated to such an extent that only the green to yellow (respectively orange and red) have an effect on erythrosine or cyanine plates, while only a weak effect is noticeable in the blue (see Fig 3 and 6, plate)).

On plates, which are colored with Sensito green or Benzopurpurin, the green and yellow sensitivity (respectively red sensitivity) predominate, but the sunlight that has passed through yellow glass is influenced in its intensity distribution of the colored rays in such a way that the violet up to Orange can be depicted photographically approximately as a continuous band \*) (see Fig. 4, panel I). So if it is a reproduction of the spectrum from H to above D, benzopurpurine plates with a yellow disk would be the same; Under these circumstances, Sensito green works up to C (see Fig. 5).

In many cases, however, it is preferable to use erythrosine or the like plates without a slant instead of a shorter exposure.

Red glass in front of the slit of the spectral apparatus is very suitable for photographing the red spectral area of bright light sources. Red flashed glass (copper oxide glass) mainly leaves

1) The absorption spectrum of the chrysoidin solutions is usually incorrectly stated. This is how StebiDins found, for example. that its absorption of blue rises evenly above the violet, even slightly increasing in the violet. The photograph of the absorption spectrum shows the opposite, in that the absorption towards violet decreases rapidly. The reason for these contradicting data lies in the fact that the

observation of the absorption spectra in the violet part with the eye is much less reliable than the photographic recording. Very slight light attenuations in violet often appear significant to the eye when observing broad absorption strips and one can be tempted to draw the absorption curve upwards. Not only with chrysoidine, but in many similar cases, the photographic method alone gives correct results when it comes to the more breakable end of the spectrum. I am now re-examining a number of substances from these points of view.

2) Diffuse light comes into the spectrograph through the multiple reflection of the light from lenses and prisms, etc. In photographic recordings of the solar spectrum, the scattered light is often noticeable in a very disruptive manner, as it often occurs in the red or other less light parts of a spectrum causes a general weakening of the bromide silver layer before the faint spectral lines appear. This obstruction occurs most strongly when a light source contains a large number of intense blue rays in addition to a few red rays. Here the action of the red rays occurs I always back against that of diffuse blue light; If, moreover, the plates are not very sensitive to red and very sensitive to blue, as is the case with normal bromide silver plates, the deficiency only becomes worse and the entire image area is blackened evenly. Plates sensitized for orange and yellow are far better, although yellow or red glasses are also beneficial.

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3) Yellow overhanging silver glass absorbs only violet up to 7 instead of blue, but lets a lot of ultraviolet through.

+) A minimum at E emerges more or less

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only light from the Fraunhofer line D to the outermost Roth can penetrate. The more breakable rays are not all evenly and strongly absorbed, but with a very strong light effect one notices the passage of blue rays (G to F). The ultraviolet part as well as green and yellow (from F to D) are completely absorbed; but yellow light at D- already partially penetrates.

By excluding all alien light, the red part of the spectrum can be photographed reasonably well even on ordinary bromide-silver gelatine plates; yes, Draper could even photograph infrared under favorable conditions.

Rothe glass screens, however, can only be used with full success (with the solar spectrum) if the plates have been sensitized to red with cyanine (Schumann), sensitogreen or cerulein (or other red sensitizers)(see cerulein plates behind red glass Fig. 10, panel II .)

Of course, various other colored screens can be used in the same sense as indicated here (e.g. for yellow liquid screens: methyl orange, tro-

paeolin etc.).

The photographic operations involved in making spectrum photographs.

Although the photographic operations are essentially the same as for the production of other photographs on bromosilver gelatine, it still seems important to me to go into those working methods which are in my hands in the production of many hundreds of. Spectrum photographs have proven best;

a photographic spectrum image has to be produced after every usual development process, but such images either lack the intensity and power of the lines or the entire spectrum image blurs into an excessively opaque strip in which all delicacies and details of the lines are buried.

1. Set up the darkroom. It should be spacious and completely darkened so that even after a quarter of an hour's stay (where the eye is receptive to weak light impressions) a glimmer of daylight is nowhere to be noticed. The room should be dry and possibly have light-tight ventilation.

2. The darkroom is illuminated with a dark red lantern, one half of which is covered with brown tissue paper, so that the red light that brushes against the plates sensitized in dyes is still strongly attenuated.

The usual bromide-silver gelatine plates can be viewed without concern in the direct red light and written on (signed) with a soft pencil (on the gelatine side). But silver bromide plates are never left open in red light for long periods of time.

Sensitized plates should only be exposed to subdued light and this too as little as possible.

3. Choice of bromide silver plates. For this purpose all good commercial silver bromide gelatine plates, which are used by the photographers for the production of portraits etc., are suitable. The inexperienced person is determined to make his own PBrom silver gelatine plates

discouraged, as it would only increase the uncertainty of his results.

Ä ±) cf. Eder's "Photography with silver bromide gelatine", 1886, Halle a. S. (III. Vol. Of "Detailed Handbook of Photography").

?) However, it is not entirely irrelevant which drying plates are sensitized with dyes. Plates rich in iodine are generally less suitable for the production of plates sensitive to red using cyanine etc. than pure silver bromide plates. Since, however, the "silver bromide gelatine plates" on the market almost never contain more than 2-3% iodized silver, physicists and chemists who do not want to get involved in special photographic studies can safely buy any commercially available silver bromide. Use plates as soon as they have good sensitivity (18-23% of the Warnerke sensitometer).

Photograph of the spectrum Cover the immersed plate quickly and evenly. Of course, the prepared layer of 'the plate' (the bromosilver layer) must face upwards; if it were to lie against the ground, it would be rubbed and imperfectly soaked. |

Bathing takes 3-5 minutes. You then take the plates out, let them drip off a little and place them on a so-called "plate stand" to dry, whereupon the plates dry fairly quickly. No direct red light (possibly no light at all) should fall on the panels while bathing and drying.

5. It shouldn't take too long to dry. The plates can only be kept for a few weeks?).

6. Exposure of the plates in the spectral apparatus. It must be determined empirically. Best to. Recommend that deeroger try four different exposure times, for example 1.210., 60 seconds, g (with sun or electric light) and then, if you think you have determined the correct time, to do every further experiment with two exposure times, which are 11 /, times to double apart.



7. The evocation (development) of the image. The invisible light image does not need to be produced immediately after exposure, but can take place several days (even several weeks) later. At least I advise, as soon as plates are used which have been sensitized in ammoniacal ink baths, to develop them soon after exposure and not to leave the plates undeveloped for longer than a week, otherwise the plates could become foggy.

Of the many developers that are possible with silver-bromide gelatine plates, the "iron oxalate", the "potash" and the "soda developer" prove to be useful for our purposes).

At the moment I am working exclusively with the soda developer, who provides me with delicate and intense images as required and keeps the plates very clear.

Two solutions are made:

A. Pyrolysis. 100 g neutral sulphurous soda and 148 pyrogallol are in 500 cm<sup>3</sup> Dissolved water and added 10 drops of concentrated sulfuric acid, which increases the shelf life of the solution. This solution can be kept in sealed bottles for several weeks.

B. Soda Solution. 50 g crystallized pure soda are in 500 cm<sup>3</sup> Dissolved in water. Immediately before use, mix:

20 cm<sup>3</sup> Pyro solution 202. Soda solution AU \ Nasser and 3-4 drops of potassium bromide solution (1:10).

The effect of this developer can be modified. If you take less water (for example 20 cm<sup>3</sup>), The resulting image appears stronger, more intense. If you take more water (for example 60 cm<sup>3</sup>), the image appears very delicate and thin and is usually closed for spectral purposes monotonous.

1) If the panels are placed on a sheet of blotting paper against a wall, they dry more slowly and more unevenly than on a panel stand, where air can enter from all sides. |

2) Ordinary silver bromide gelatin plates will remain unchanged for many months. In the ammoniacal dye bath, however, the durability of most panels is impaired, so that after 2 weeks one can no longer count on the unchanged properties of the panels with certainty (see especially with cyanine).

2) cf. about this Eder's "Photography with bromosilver gelatine", 1886 (Halle

a. S.). 66 J. M. Eder.

The potassium bromide acts as a retarder. It slows the evocation but keeps the plates very clear; the unexposed areas of the bromide silver should remain completely white in the developer.

Cyanine plates, which contain ample ammonia in the dye bath, often require 10 to 20 drops of potassium bromide solution. But then you have to develop twice as long. You keep swirling the cup during development.

The development takes an average of 2-3 minutes if the photographic spectrum was very bright; on the other hand 5 to 10 minutes if it was faint. Faint spectra, for example from Geissler's tubes, require special care when developing, so that the faint impression of light can be made visible).

The picture is assessed by taking the plate out of the developer and holding it against the red lantern. During the other time you cover the development cup with a cardboard lid so that no light can enter. The faint red lantern light would also decompose ("disguise") the red-sensitive cyanine plates. |

8. After the image has appeared strong enough in the developer, it is rinsed a little in a bowl with water and then placed in an approximately saturated solution of alum for 1–2 minutes. The alum bath strengthens the layer and removes the yellowish tint that adheres to the gelatin layer from the pyrogallol bath.

9. The plates are now coming, etc. 65

| 4. Bathing the plates in the dye solutions. The dye solutions should be filtered

and are so abundant in pure porcelain or glass cups that the immersed plate is completely covered.

Move the cup to make the solution die

into the fixer. It consists of a solution of sodium hydroxide in about 4-6 parts of water. As soon as the silver bromide has dissolved and all milky cloudiness has disappeared. (which takes 3–10 minutes) the plate is fixed. It is better to leave the plate in the fixer for 5 minutes too long than for too short a time. If the gelatin layer does not adhere firmly to the glass, mix this fixer with the same volume of saturated alum solution; the bath becomes cloudy (excretion of sulfur) and is used after a few hours; it can be used for 8 positions. The shift holds up very well in the mixed bath.

10. After fixing, the plates are brought into the daylight, rinsed well under the tap, placed in a bowl with pure water and rinsed (with frequent water changes) for half an hour, rinsed again and then standing upright (on a Record stand) dried.

Drying takes half a day.

11. The finished plates should be painted with "negative varnish" and never unpainted for copying used or kept. Such photographer negative varnish can be bought anywhere.

Methods for sensitizing the silver bromide gelatine for individual spectral regions. Erythrosine plates (see Fig. 2 and 3, panel I).

Good, sensitive, commercially available silver bromide gelatine plates are bathed in an ammoniacal solution of erythrosine (tetraiodofluorescein potassium, also called bluish eosin or iodeosin).

!) For very faint spectra I recommend the following mixture: 20 cm<sup>3</sup> Pyrolytic solution 20 g Soda solution 20 g Water. I don't add potassium bromide; only in the event that plates "obscure" themselves in this developer do I add a few drops of potassium bromide.

Photograph of the spectrum, etc. 67

The erythrosine should be pure; That means it should not contain any additions of common eosin (tetrabromofluorescein potassium or sodium) or other coloring agents and no tremendous iodine salts.

Erythrosin (iodoeosin) differs from common eosin (bromeosin) in that the aqueous solution of the latter fluoresces yellow-green, but the solution of the former does not fluoresce. |

All types of erythrosine on the market sensitize the bromide silver to green and yellow, but not all to the same degree).

The erythrosine bath is prepared as follows:

100 cm<sup>3</sup> Water 1 g Erythrosine solution (1: 400) 2, 2 mmontelke (d = 0.9).

This solution \*) is put into a flat porcelain cup about 1 cm high, put the silver-bromide gelatine plate (with the coated layer facing upwards) in it, move the cup a few times so that the liquid floods the plate well everywhere. The plate remains in the bath for 3 to 4 minutes (approx).

It is then lifted out and dried in the open air on a so-called flap stand. Warm dryers are not well suited for this. It is best to let the damp plates dry freely in the completely darkened darkroom. The drying should be finished in 5-12 hours; places which remain moist for a long period of time are usually marked on the finished photographic image.

The silver bromide gelatine plates dyed in the ammoniacal erythrosine bath are notably more sensitive (both to white light in general and to green and yellow light in particular) than silver bromide layers, which you get when you add the silver bromide gelatine to the presentation mixed with erythrosine in a warm, molten state and thus covers the glass plates).

In addition, it is more convenient for the experimenter to buy ordinary (non-dyed) silver bromide gelatine plates and then sensitize them with suitable dyes at will.

The erythrosine plates are about as sensitive to white light as the original plates were; sometimes the sensitivity has even increased a little. However, green and yellow light have an extraordinarily much stronger effect on erythrosine plates, while a loss of sensation

possibility in blue, violet and ultraviolet is not noticeable in photographic spectral recordings).

1) Dr. Schuchardt in Görlitz.

2) Increase of the erythrosine content in the above regulation to 11 g / 100 cm<sup>3</sup> is cheap for some records; in others this reduces the overall sensitivity of the colored bromide silver, but causes the sensitization maximum to emerge somewhat more strongly in the green and yellow.

3) A larger amount of ammonia (for example 10 g / 100 cm<sup>3</sup>) Increases the overall sensitivity of the plates not insignificantly. Some bromide-silver gelatine, however, do not tolerate such large amounts of ammonia, instead it decomposes and gives hazy images. If the plates can tolerate more ammonia without damage, one can benefit from this increase

make use of sensitivity.

4) The dye bath can be used in different ways. Also recommended (Dr. Mallmann and Scolik's method, Photographische Correspondenz, 1886, p. 140) is a 100 cm pre-bath? Water and 1cm? Ammonia, wherein the plates soak for 2 minutes; this is followed by the dye bath, which consists of 100 cm<sup>3</sup> water, 4 cm<sup>3</sup> Erythrosine solution (1: 400) and 2cm<sup>3</sup> There is ammonia (duration of this bath 1<sup>st</sup> /, Minutes).

5) Too short a bath time causes imperfect coloring of the layer. After an excessively long bath time (10- 15 minutes) the gelatin layer would absorb too much dye, which would damage the overall sensitivity to light.

6) This statement was first made by V. Schumann and it has been generally accepted since then.

7) A closer comparison reveals that the usual silver bromide plate is a little more sensitive to blue and violet than the erythrosine plate, but this is of no relevance in practice.

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Benzopurpurine plates (Fig. 3, panel 1).

To study absorption spectra, for which I have sufficient light, I use benzopurpurine plates. The same are a little less sensitive to white light than erythrosine plates, they are also relatively less sensitive to green and yellow light than erythrosine plates, while their sensitivity to blue is predominant. Nevertheless, the benzopurpurine plates show the advantage that they reproduce the region of E<sub>B</sub> D<sub>1</sub> /, C more evenly as a broad sensitization band, while erythrosine produces a more intensive photographic effect that rises to a strong maximum at 2% Dr.

I use benzopurpurine plates as soon as I have to examine the absorption spectra of sunlight in dye solutions etc. in the districts E to above D.

To photograph faint emission spectra, I prefer erythrosine plates (for green to yellow) or cyanine plates (for orange and red to C). The following is recommended as a benzopurpurine bath:

100 cm<sup>3</sup> Water | 2<sup>nd</sup> Æ aqueous benzopurpurin 4 B solution (1: 400) 1, Æ "1 cm<sup>3</sup>

Ammonia. Benzopurpurin 4B can be obtained from the aniline paint factory formerly

Bayer in Elberfeld. Cyanine plates (Figures 6 and 7, Panel I).

"Cyanine plates" are produced by bathing silver-bromide gelatine plates in an aqueous-alcoholic solution with the addition of ammonia. Such plates show an extraordinarily increased sensitivity to orange and red and must therefore be produced with great care. When bathing the plates, only very dark red light may be used, and a screen made of brown translucent paper should be placed in front of the red lantern; it is best not to let any light fall on cyanine plates while bathing and drying. I use the cyanine bath in the same way as I described it in December 1884!), Namely:

100 cm<sup>3</sup> Water 2<sup>nd</sup> Æ alcoholic cyanine solution (1: 400) He, eimmonialk<sup>2</sup> ± Id 20:91):

This mixture must be filtered through pure paper?) And used quickly, because it soon fades in the light and then partially loses its effect. The alcoholic cyanine solution should also be kept in the dark and not be too old at all if it is to demonstrate its full effectiveness - I make the solution fresh every 8 days.

The plates remain in the bath for 4 minutes with constant swirling, after which they are left to air dry voluntarily. |

The cyanine plates have a lower overall sensitivity than normal bromide silver plates or erythrosine plates and must, depending on the circumstances, be exposed 2 to 5 times longer?) If all parts of the spectrum (for which they are sensitive at all) should reproduce.

By increasing the addition of ammonia in the above bath to 1 to 2 cm<sup>3</sup> the sensitivity of the cyanine plates can be increased, but then the photographic images usually become hazy.

!) Comp. pag. 1 of these treatises. ?) Schumann recommends filtration through glass wool.

?) I already had cyanine plates in my hands, which were more than 10 times less sensitive to white light than silver bromide plates. |

Photograph of the spectrum, etc. 69

The somewhat more cumbersome Schumann's staining method ') also gives very good results. He first places the plates in a 1 /, 2 cm<sup>3</sup> Ammonia and 100 cm<sup>3</sup> Water in which the layer loosens. After two minutes they are taken out and bathed in a mixture of 100 parts water, 1-2 parts ammonia, 5-10 parts alcohol and 2-5 parts more alcoholic

Cyanine solution (1: 500). The higher alcohol content of the cyanine bath prevents it from decomposing too quickly.

settlement. However, since liquids rich in alcohol penetrate the gelatin layer with difficulty, the layer is loosened by the ammoniacal pre-bath. The cyanine plates can be kept for 8-14 days. Names

every day in summer they change when they are kept for a long time;

show it then there are irregular reductions in the developer and a "veil" occurs?).

Sensito green plates (Fig. 5, panel)).

The green made from paraoxybenzaldehyde and dimethylaniline?) I want to call it "Sensito green" for the sake of brevity, because it is very sensitive to alkalis (it turns a deep purple color) and is also a good red sensitizer for bromosilver gelatine.

As a result of this dye, bromide silver becomes very sensitive to yellow and red, in that, similar to cyanine, a broad sensitization band extends from green to above C, which rises to a broad maximum before D to towards C).

This dye by no means makes the silver bromine more sensitive to spectrum orange or red than cyanine; I have not yet succeeded in definitely increasing the red sensitivity of bromide silver (compared to blue sensitivity) to the same extent as can easily be done with cyanine, but in spite of this, the sensitizer gives

bromide silver properties which make it a valuable tool for the spectrophotography of high-intensity spectra. | The solar spectrum can be photographed very well through yellow glasses on sensitive green plates, whereby the blue part and the orange part are obtained with approximately the same intensity on the photographic negative.

As a bathroom I use: 100 cm<sup>3</sup> Water, A cm<sup>3</sup> (or 3â€”5 cm<sup>3</sup>) Sensito green solution in alcohol (1:400),!

/, cm<sup>3</sup> Ammonia (up to 1 cm<sup>3</sup>).

This purple solution needs to be filtered and will be used soon. The alcoholic solution can be kept for many weeks; the mixture mixed with water and ammonia spoils after a day.

The dried plates can be kept for several weeks.

I think sensitive green sheets are very suitable for certain purposes of astronomical photography, for example the sun through red glasses. Since only a narrow spectral region comes into play here, errors due to inadequate achromatism of the telescopes are eliminated. However, similar results can certainly also be obtained with other plates sensitive to red (for example cyanine

plates).

1) Photographisches Wochenblatt, 1885, p. 395 and 1886, p. 49 (also Dingler's Polytechnisches Journal, 1886, vol. 258, p. 320).

2) In other words, a plate with a "veil on the edge" is reduced in the developer even without previous light effects, especially at the edges of the plate. Over time, the edge veil advances towards the center and finally the entire plate is unusable.

3) S. O. Fischer's Annual Report on Chemistry, 1881, p. 452 and reports d. German. chem. Society, 1881, p. 2522.

4) In the case of a weak color, little of this maximum is noticeable, but only a moderate continuation of the light effect from blue-green to orange. With stronger coloring, the effect of the yellow and red rays is increased within the specified limits and the spectral lines are very sharp. If there is an excessive addition of dyes, the overall sensitivity to light generally decreases.

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Cerulein plates (Figs. 10 and 13, panel ID.

The previously described red sensitive plates show their strongest effect in the orange and red of the Fraunhofer line D to C. Am. The most sensitive to these rays are the cyanine bromide silver plates, followed by the sensitive green plates, which reproduce the spectral lines particularly sharply; further sensitive to the external red were silver bromide plates colored with Bleu Coupier and other dyes, which were described in my earlier treatises).

Here, however, attention should only be drawn specifically to cerulein, which served me the best of all preparations for photographing the red end of the spectrum - from D to over A into the infrared.

Coerulein plates give this district a uniformity and sharpness which is highly satisfactory. |The cerulein bath is made as follows:

Manlese-r Theil Coerulein.s. (water-soluble obtained from Dr. Sebuechardt in CiHiz in 100 parts of waterand mixes this solution immediately with ammoniacal water in the following proportions:

100 cm<sup>3</sup> Water 1â € "1! /, Cm<sup>3</sup> Cerulein.S solution (1: 100) "%, (to. Dem<sup>3</sup> Ammonia (ad =. 0:91).

This beautiful green, clear liquid is immediately used as a bath for highly sensitive bromosilver gelatine plates for 4 minutes without hesitation. Low sensitivity plates are not suitable for this process?). The bathed panels should be dry in 5-6 hours.

The cerulean solutions are not durable; they often decompose after an hour and then become cloudy. The cerulein bromide silver plates show a high sensitivity to blue light. The Li

On the other hand, sensitivity to red light is not so great and in regions D to C it lags far behind cyanine. On the other hand, if the solar spectrum is photographed after dark yellow screens (chrysoidal solution screens, Fig. 13) or red copper oxide glass (clad glass screens, Fig. 10) have been pushed in front of the slit, the peculiar sensitizing effect of cerulein emerges: - That | The photographic spectrum image appears sharply defined after a sufficiently long exposure from C to above A and in particular the area from D to above A can be photographed behind red glasses with the incomparable sharpness of the Fraunhofer lines.

It should be noted, however, that the exposure time under these circumstances can be 1, 2, even 5 minutes in direct sunlight, while erythrosine plates are exposed in a second and cyanine plates only need to be exposed for several seconds under the same circumstances

I therefore expressly recommend the cerulein plates only for photography of the red part of the spectrum, as soon as strong light sources are available and the rays of the lowest refractivity are to be shown in the visible spectrum and the beginning of the infrared.

Incidentally, the fact that cerulein plates?) Also show a somewhat increased sensitivity to blue and (without yellow or red screens in front of the

Column) also good for photography of the ultraviolet, violet, and blue parts of the spectrum

1) cf. pp. 26 and 41 of these treatises.

2) The silver bromide gelatine plates should show at least about 20° on the Warnerke sensitometer; such plates are now easily obtained from the dealers of photographic commodities.

Â®) This applies not only to cerulein, but also to other dyes; these then prevent the blurring of the lines, which is not uncommon with ordinary panels (without the addition of colorants) when there is plenty of light, as I pointed out earlier. However, not all dyes have the same beneficial effect on the sharpness of the lines.

Photograph of the spectrum, etc. 71

are suitable in that they bring about greater sharpness of the lines; but then the pictures are colored a little stronger (11), cm? Color in the above regulation). No longer exposure is necessary for the photography of the blue spectral region, and that

Sun spectrum sufficiently exposed in a second.

About the suitability of silver bromide gelatine plates for precise measurements.

The measurements of the position of the photographed spectral lines or strips should be made on the glass plate and not on photographic paper copies. The paper expands unevenly during its treatment with the silver, fixative, and wash baths. If the paper (albumen paper or salt paper) is left to air dry voluntarily, the warping of the same is usually hardly noticeable with a short length of spectral recordings. The length of the paper alone changes very significantly if it is affixed to cardboard with paste or some other adhesive by brushing and pressing. This distortion (expansion) can be  $2 \times 10^{-4}$  /, the original length; this is an amount which is inadmissible for the determination of the location in the spectrum, even with low demands on accuracy. Measurements on photographic paper copies should therefore be avoided. |

Measurements about location determinations on spectrographic glass images, however, offer a completely satisfactory accuracy. I checked bromosilver gelatine plates a long time ago (with the help of photographed nets) for any distortion of the layer and none of the

samples were looking for a distortion which could have reached the amount of).

Hasselberg has also shown in a series of spectrophotographs on bromosilver gelatine and extremely precise measurements of the position of the same on the glass negatives that the accuracy of the determination of the wavelength can be achieved in five places? meets the highest requirements.

However, this only applies if the bromide silver gelatin layer is firmly adhered to the glass. If the gelatine, which was used to produce the emulsion, was not solid, but was in the warmth at the beginning of the decomposition due to digestion that was too long, the image layer in the baths can stand out from the glass in bubbles, which then dry unevenly. If such bubbles appear, which occur in particular during washing after fixing in the case of bad bromosilver gelatine plates, the recording is unsuitable for precise measurements. The presence of such bubbles never escapes the observer's eye, as they protrude like the heads of large pins and can reach the size of peas. '

But another circumstance becomes

usually less noticed. Some bromide-silver gelatine plates do not have a smooth surface, but a wavy structure, which may be due to the fact that the warmed gelatine emulsion is no longer completely liquid when it is poured onto the glass plate, but rather

was half frozen. Such plates. do not give the straight spectral lines straight, but wave-like

1) Eder's "Detailed Handbook of Photography", Vol. II, p. 25.

2) Hasselberg writes in the annal. d. Physics and Chemistry, New Series, Vol. XXVII, 1886, p. 415: "One might suspect given the many and long-lasting washes to which a gelatine plate has to be subjected to



produce the image It is possible that a displacement of two photographic Spectra placed one on top of the other can be caused by distortion of the skin during drying. However, several experiences speak against such an assumption. First, Eder tested the stability of the layer for gelatine plates without discovering a distortion reaching the amount of  $\frac{Y}{1000}$ . Second, if there was any noticeable distortion, the spacing of the lines of the solar spectrum on different plates would be different. However, within the limits of the possible accuracy of the measurements, this is not the case. Hasselberg has a table of his measurements in the group of sun lines at  $\lambda = 4653: 70$ , which confirms this information. |

7 J. M. Eder, photography of the spectrum etc.

crooked again. Even with a weak magnifying glass, this wave-like distortion can be detected and such plates can be eliminated. I conclude that the obstruction stems from the preparation of the plates and not from the type of development and fixation from the fact that, among a few hundred plates, only three or four of the same wave-like curvature of the lines showed, while others immediately or earlier later plates made the lines straight. If an alum bath is used between developing and fixing, or even better a mixed fixing and alum bath, the gelatin layer is tanned in such a way that the greatest possible security |

against the warping of the layers is given.

Usability of the dye-sensitized silver bromide gelatine plates for various optical or astronomical purposes.

The plates, which are made sensitive to green, yellow or red, are naturally suitable for photographing all those light sources that are rich in these rays (that is, "optically bright"). Erythrosine plates are particularly suitable for photography under petroleum or gas light, for photography of yellowed documents and papyrus, for microscopic photography of yellow-colored microscopic specimens, for recording clouds in the blue sky after the blue has been suppressed with yellow Glasses. Since the many stars have a reddish light and their green and yellow spectrum is very intense, it was to be foreseen that erythrosine plates would have to be very suitable for astrophotography of such objects, which Dr. Lohse at the astro-physical observatory in Potsdam?) And Mr. Director Gothard at the astro- physical observatory in Hereny have been convincingly proven by careful experiments. The same is to be expected with lunar photographs.

Poorly achromatized telescopes can probably be used for photography if one excludes all other rays with red glasses and then takes the photograph with cyanine, azaline or other red sensitive plates.

Direct solar photographs turn out sharper and sharper on plates that are labeled with Bleu Coupier or Coerulein Ben and there is less of a risk of overexposure.

The suitability of sensitized "orthochromatic" plates for the reproduction of paintings is known.

!) Dr. Mallmann and Scolik even put portrait photographs in very short exposure times on erythrosine plates

here. Azaline plates work in a similar way. 2), Was made by me a "years ago ee he Die k. Hof- undStaatsdruckerei in Vienna uses the «ortho-

chromatic "procedures for this purpose extensively. 3) S. Astronomical

News, 1886.Explanation of the collotype panels (panels I and II)

according to Spectrum photographs on silver bromide gelatine plates placed in various ways.

For a clear assessment of the efficiency of silver bromide plates, which have been sensitized for different spectral colors according to the specified methods, a number of my spectral photographs have been reproduced in collotype. They are included as panels I and II. If, by repeating the methods I have indicated, ignoring the necessary precautionary measures, other researchers should not immediately achieve the results described in the treatise to the same extent, ei

A look at my photographs') more clearly than it is possible with many words to clearly show the result I have achieved. These photographs do not lay claim to a perfect reproduction of all existing lines; they are nothing more than evidence of the spectral regions in which the sensitizers increased the light sensitivity of the bromide silver.

These documents show a small selection from my research series. I have no doubt that other experimenters with individual dyes will achieve even better results in increasing color sensitivity if they study one or the other dye in detail and determine the most favorable experimental conditions under the respective circumstances.

The Steinheil's large spectrograph with three prisms was used for my investigations, which is illustrated and described on page 5 of these treatises.

Fig. 1, panel I shows the photograph of the solar spectrum on ordinary silver bromide gelatine. Exposure time about 1 /, second. With a longer exposure the effect would extend as far into the ultraviolet as any other photograph shown here, but the clarity of the Fraunhofer lines in the blue would have disappeared.

Fig. 2, panel I shows the solar spectrum on erythrosine plates. Exposure time 1 /,  $\hat{a} \in "1 /$ , second. The ultraviolet to blue spectrum image is roughly the same as the previous one, but the sensitization maximum occurs between E through D. Line D is still clearly visible on most of these images?).

Fig: 3, panel I shows the effect of a yellow glass in front of the slit of the spectral apparatus on erythrosine plates. Exposure time 1 second. The ultraviolet and violet have almost no effect in this short exposure, the blue weakly; on the other hand, the green and yellow in front of E to D stand out very strongly. Such plates are suitable for "orthochromatic" photography, the effects in yellow and green outweigh those in blue and violet. |

Fig. 4, panel I is recorded on a bromide silver plate stained with benzopurpurin 4 B (with a yellow glass pane). The band of sensitization is broader, but less intense than that of erythrosine plates. The effect of the spectrum is fairly even from orange to violet (the dye Congo has a similar effect).

Fig. 5, panel I shows the effect of the sensitive green plates. I applied them with yellow glass. You usually have to expose longer than with cyanine plates because the relative orange sensitivity is lower. Despite the yellow glass, the effect in this picture is no stronger in the orange than in the blue. The Fraunhofer lines stand out sharply and clearly.

1) They are of course free from any retouching. Not even dust spots have been covered, which could have been done without harming the accuracy. 2) Bromeosin or other types of eosin do not work so well on quantitative color sensitivity.

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Fig. 6, panel I shows the spectrum image on cyanine plates with the inclusion of yellow glass. Exposure time 4 to 8 seconds. Since the relative orange sensitivity of cyanine plates (compared to blue sensitivity) is not as great as that of erythrosine plates, the exposure had to be longer than with these. As a result, besides orange, more of the blue rays came into effect, so that the photographic effect can be followed up to over M.

Fig. 7, panel I is the photograph of the solar spectrum on a cyanine plate (exposure time 2 to 10) seconds. This longer exposure made the ultraviolet effective. In the green there is a minimum of effect; at D to C (and to B) a maximum.

Fig. 8, panel II. Silver bromide plate colored with green from toluene aldehyde. Exposure time 2 minutes behind yellow glass. Also serves as a typical example of the sensitizing effects of methyl green, brilliant green, etc.

Fig. 9, panel II. Silver bromide plate colored with Bleu Coupier?). Exposure 1 to 5 minutes. These photographs show very clearly the difference in the effect of yellow glass (Fig. 9) and chrysoidine tubes (Fig. 12). In the first case, the ultraviolet is weakened, although the enormously long exposure of this area still has some effect. When the chrysoidine screen is used, the ultraviolet and violet appear almost undiminished, while the blue and green are suppressed. The lines from green to red are more prominent. In general, the sharpness of the lines on the negative is great. (You can see this particularly in Fig. 9. On the original negatives, all the spectra are drawn much more sharply than on the paper copy!)

Fig. 10, panel II. Solar spectrum on a cerulein plate behind red glass. Exposure 1 to 5 minutes. It lacks: ultraviolet, violet; some blue comes into play, green and yellow are missing. From D to over

A the spectrum appears very intense and with sharp lines (A, a, B, C).

FIG. 11, panel II is the spectrum image attached for comparison on ordinary silver bromide gelatin (without added dye) behind chrysoidine screens. In spite of longer exposure, the effect in the less frangible part is far behind in comparison with cerulein plates; but you can still see the effect far into the orange, which is not so clearly possible if you work without an umbrella.

Fig. 12, panel II shows a plate sensitized with Bleu Coupier behind a chrysoidine screen. This dye has already been described in more detail on pages 45 and 50.

Fig. 13, panel II shows a cerulein plate behind a chrysoid screen. Except for the suppressed blue area we find the whole spectrum photographed from ultraviolet to over A. Exposure time 90 seconds. This plate

reproduces all spectral regions well. In the production of the collotype lines A, a, B, C were given special consideration and the copy was not exposed for so long that the lines in the other areas were copied enough, which is why the areas in question appear white. The entire spectrum of lines is visible on the original negative.

Figures 14 and 15, Panel II show the utility of erythrosine plates for photography of faint spectra. The upper half (Fig. 14) is the so-called Swan's spectrum (blue part of the Bunsen's flame). Exposure time 12

- 36 hours. Below is the spectrum photograph of burning magnesium for comparison. The effects range from D to ultraviolet. The maximum of sensitization emerges unmistakably. In Swan's spectrum, groups of lines in green to yellow appear in the photograph that could no longer be photographed on ordinary plates.

Thereby the suitability of the photographic-spectroscopic methods described here is sufficiently proven.

|

) The ultraviolet would have had an effect on normal plates or erythrosine plates to the same extent after longer exposure.

?) Comp. p. 41 of these treatises.

Plate I.

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Photographs of the solar spectrum on silver bromide gelatine and variously sensitized dry plates.

latte behind yellow filter.

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bar. â € "3.

Erythrosinp

2. Eryth Benzopurpurin 4 B colored bromide silver gelatine plate behind a yellow filter.

1. Ordinary silver bromide gelatin

plate. -Sensito green sheet.

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â € "6. Cyanine plate behind yellow filter. - 7. Cyanine plate,  
Collotype of the k. k. Graphic teaching and research institute in Vienna.

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Plate U.

Photographs of the solar spectrum on gelatin and silver  
bromidevariously sensitized drying plates.

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13th

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8. Bromosilver gelatin plate, colored with green from toluic aldehyde. â € "9. Bromosilver gelatine  
plate, colored with Bleu Coupier. â € "10. Cerulein plate behind red glass. â € "11. Ordinary silver  
bromide gelatine plate (without added coloring) behind a chrysoidine screen. â € "12. Bromosilver  
gelatin plate, sensitized with Bleu Coupier behind a chrysoidine screen. â € "13. Cerulein plate  
behind a chrysoid

screen. â € "14, 15. Swan's Spectrum and Spectrum of Burning Magnesium on silver bromide gelatinplates.

Collotype of the k. k. Graphic teaching and research institute in Vienna.

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Photochemical phenomena and the undulation theory of  
light.Of

J. M. Eder. :

From a lecture by the author occasionally at the Daguerre celebration of the Vienna Photographic Society on October 15, 1889.

If we observe the scientific attempts to explain the photographic evoking processes of the invisible light, which have been discovered since Daguerre, the simple attempts at explanation at the time of the invention of the daguerreotype, which condense the mercury vapors according to the Moser principle, stand out Explain the breath images. Analog would be the attraction of delicate silver sludge from the developer liquid when developing a wet Collodion plate, but with which the inadequacy of that all-too- simple view comes to light. Both development methods do not seem to allow going beyond a certain limit of sensitivity. The achievement of the highest light sensitivity was reserved for the chemical development process of the bromide silver, in which the bromide silver molecule affected by the light is reduced itself in the developer. The sensitivity limit reached up to now does not seem to be able to be exceeded by changing the developer substance, because the most diverse bodies (iron oxalate, hydrosulphurous acid, pyrogallol, hydroquinone, pyrocatechol, amidonaphthol sulfonic acid sodium ,

Paraphenylenediamine) give pretty much as a developer d

same degree of sensitivity of the bromide silver plates. Attempts to make the bromosilver molecule itself more suitable for interaction for light and chemical decomposition were more favorable. |

The modern optics are based completely and with overwhelming certainty on the undulation principle of light. It seems of importance to explain the photochemical phenomena together with the newly discovered color sensitizers according to the same principle and to consider the modern view of the wave movements of light, the inner molecular movement inherent in all bodies and the absorption phenomena.

The inner molecular movement is controlled: 1. by those forces which act from molecule to molecule, that is, physical molecular forces; 2. by those that work from atom to atom, that is, chemical forces that cause the chemical constitution or the chemical decomposition of the molecules.

When an incoming light wave is in harmony with the internal natural oscillation of the molecule oscillates, the light wave acts on the molecule and increases the amplitude of the oscillating KR 76 JMerRaver

Molecules. The light wave is consumed in the process; she did a job. Living power can be transformed into other manifestations and the absorbed light wave, as I have already mentioned in an earlier treatise!), Can induce chemical work, heat generation, etc. That interprets the former phenomenon. If we assume that the light wave increases the amplitude of the natural oscillation of the molecules very significantly, when a certain limit is exceeded, the molecular structure may tear, which means that photochemical decomposition has taken place. According to the undulation theory, the carrier of light, the ether, fills all spaces between the molecules in the atoms of the body and is forced by the internal molecular movement of the body to vibrate or rotate at the same speed and size move, of which the movements of the molecules themselves consist. The body hit by the light only absorbs those vibrations from the ether waves of its environment with which its molecules themselves are able to see or vibrate,

Let us call the spectroscopically determined wavelength of the light beam which is most strongly absorbed by a substance,  $\lambda$ , the speed of light ( $v$ )  $\hat{=}$  229,000 km and the number of oscillations of the absorbing molecules to be searched for the equation

$$N = \frac{v}{\lambda} \cdot x$$

Of absorbing substances which show absorption for various types of light rays, the most intense absorption is usually considered; this characterizes the main vibrations of the Molecule, as well as - according to a good parable by Dr. KrÃ¼ss  $\hat{=}$  "the most intense vibrations of a tuning fork or string produce the characteristic main tone of the same. With a tuning fork, the larger the amplitude, the louder the tone; in the light the intensity increases. One can conclude that a greater intensity in the absorption of light is caused by a greater amplitude of the oscillations of the molecules in the absorbing medium.

Silver bromide in the form of gelatin emulsion shows the maximum absorption for light of a wavelength

$\lambda = 450 \mu\text{m}$ ; from this it is calculated according to the above formula that the molecule of the bromosilver requires 664 trillionths of a second to execute a main oscillation. In fact, light of the same frequency acts most strongly on bromine-silver, in other words, it increases the amplitude of the internal molecular vibrations of the bromine-silver so strongly that a breakdown of the molecule occurs or begins, which the photographic developers continue so that there is a strong reduction.

In addition, there are also numerous secondary vibrations which, inside the bromine-silver molecules, cause the bromine-silver to absorb other light waves with a longer or shorter number of vibrations, whereby the light is consumed. However, since these secondary vibrations are less powerful and can therefore interact less with the light waves, more intensive light is present: so that the vibration and amplitude of the internal molecular vibrations increases until the molecule ruptures, with In other words, the silver bromide has a low light sensitivity to such rays. For example, light from the extreme red to the extreme ultraviolet is absorbed by the bromide silver, but to a lesser extent and the photochemical process also takes place to a lesser extent.

The low sensitivity of yellow or red bromide silver is well known; it becomes larger when the bromide silver is digested with ammonia and so on; for example, bromide silver is only curdled

according to degrees of yellow-green light, which with a wavelength of 563. (corresponding to a Schwin-

duration of a 531 trillionth of a second) oscillates, changes.

1) cf. pag. 1 of these treatises.

Photochemical phenomena etc.

TR

This light is also absorbed to a small extent; it is the internal movement of the bromide-silver molecule only with secondary oscillations in harmony with the mentioned light rays and the light with the oscillation number of 531 trillionths of a second can only with difficulty increase the amplitude of the oscillations of the bromide-silver molecule up to the rupture of the atomic complex .

Let us consider the effect of another chemical substance, which forms an intimate connection - be it by chemical means or by molecular attraction - with the bromide silver and now absorbs light of 563 nm wavelength at that time and according to the previously stated Formula for the execution of an oscillation takes 531 trillionths of a second.

One such body is erythrosine; In an alcoholic solution it absorbs the strongest light of 529 nm wavelength, while the bromide silver colored with it absorbs light of 563 nm. Wavelength absorbed. If an incident yellow-green light beam of wavelength 563 nm hits the silver-bromide colored with erythrosine, he will find erythrosine molecules which vibrate most strongly in unison with the light wave and consume it. The light wave can increase the amplitude of the vibrations of the erythrosine molecule with continued exposure to the point where it decays and can, for example, bleach the erythrosine in and of itself. On the other hand, the simultaneously present bromide silver molecule can also be carried away by the increased vibrations of the dye and thereby increase the up to then secondary vibrations of the bromide silver to a main vibration and cause the disintegration of the bromide silver molecule. \

This explains why dyes that show narrow absorption stripes, that is, limit the main vibrations of the molecules to a narrow zone in the spectrum, usually sensitize more strongly because the bromosilver molecules are likely to be carried away more easily if there is a narrow attack zone.

The iodized silver is very difficult to sensitize by dye, probably because it has the main vibration corresponding to the blue rays of the spectrum and the molecular movement occurs only to a very small extent or not at all in harmony with the long-wave light rays, which is why the added absorbing dyes have the effect seems to be too weak to increase the sluggish movement of the



iodized silver molecules

to the point of rupture of the atomic complex. With bromide silver, which has a general sensitivity to different light rays, the ratio is more favorable. |

Hence the fact, which agrees with experimental observation, that the color sensitizers for silver bromide, which play such an eminently important role in orthochromatic photography, always sensitize the silver bromide in the vicinity of those regions of the spectrum which they themselves absorb.

Namely, they vibrate in unison with the light rays they have absorbed and, through the increased amplitude of the molecular vibrations of the dye, bring the bromosilver molecule into increased, harmonized vibrations, whereby the light wave increases the internal molecular movement of the bromide silver until it ruptures. As a result, the connection between the absorption of the dyes and the opaque sensibility is

sation explained on the basis of the undulation theory.

On the history of orthochromatic photography with  
erythrosine. Of

J. M. Eder.

(Photographic correspondence, 1890, page 455.)

Orthochromatic photography with silver bromide gelatine has gained considerable momentum with the introduction of erythrosine, which is the most powerful sensitizer of the eosin group and is all currently produced and marketed by the manufacturers. Orthochromatic plates contain erythrosine, although the manufacturers usually make it a factory secret. Since the introduction of the orthochromatic emulsion steered modern photography to a certain extent in a new direction, the story of the discovery of this generally accepted sensitizer is of some historical interest.

In the April issue of the *Photographische Correspondenz* of 1884, p. 95, I published a "Preliminary Communication on the Color Sensitivity of Gelatin Emulsions", which reads: "Eosin alone has little effect, but with ammonia there is a strong increase for yellow and yellow-green both wet and dry, and this applies not only to the bromeosin, which Attout and Clayton in France

I was privileged, but also from iodeosine, which has not yet been tried and perhaps the same property even more strongly.

This publication was important because Attout (called Tailfer) and Clayton had taken out a French patent (No. 152645 of December 13, 1882) on "quadruple brominated phthalein" or "eosin"; From this it follows not only that they had no knowledge of the analogous or better effect of the iodized product (that is iodeosine or erythrosine), but a new way had also been opened for the manufacturers, because this publication of mine made them independent. Became acquainted with the patented bromeosine

and without having to fear patent disputes that iodeosine could be used for the fabrication of orthochromatic plates.

On April 30, 1884 (Photographische Correspondenz, 1884, pag. 121) I followed up with a second communication, in which I described the increase in the color sensitivity of chloriodosilver by eosin to yellow-green rays.

On August 12, 1884, I described the advantages of iodeosin over bromeosin very clearly in No. 283, p. 224 of the Photographische Correspondenz, year 1884. In my ab-

On the history of orthochromatic photography with erythrosine. 79

It literally means: "I have already pointed out earlier that iodeosine!) can work more cheaply than bromeosine. Lately I've tried yellowish eosin, yellowish erythrosin ®), bluish erythrosin, rose bengal, these are all so-called eosin colors. Eosin yellowish (bromo eosin) and rose bengal showed the quantitative weaker effect on bromine and bromo iodine emulsions (with silver oxide-ammonia) than eosin bluish (iodeosin) and erythrosine. The band with the strongest "yellowing" effect was bluish with eosin and erythrosin moved further to orange than with the dyes in the yellow shade, which corresponds to the position of the absorption strips. With all these colors, ammonia increased the absolute sensitivity in general and the sensitivity in the yellow-green in particular. For example, do you bathe the plate for 2 minutes in a solution of 0:08â € "0'12g eosin, erythrosin or rose bengal at a distance of 100 cm? Water and 3cmÂ® ammonia, the strip of "yellow sensitivity" is almost twice as wide and extends much more strongly to b than without ammonia ".

This was followed by a description of my experiments with emulsions which contained eosin in the substance and described the production of ammoniacal bromosilver gelatine emulsions by adding bluish eosin (erythrosin) during the mixing of the emulsion and subsequent digestion, which I did also receive a clear sensitization in the yellow.

I not only communicated the results of my investigations into the use of dyes as sensitizers in the gelatine emulsion process in these cited papers, but also gave a long lecture on "Bromosilver gelatine and orthochromatic plates" at the ceremony of the " Association for the care of photography and related arts in Frankfurt a. M. "on September 10, 1884, an extract from which was published in Photographische Correspondenz, 1884, p. 311. At that time I not only communicated the above- mentioned results that I had published, but also substantiated the lecture by demonstrating the more important sensitizers I had found at the time, and presented a number of orthochromatic reproductions of paintings; this is proof that before September 1884 I had put the results of my photochemical studies into practice. At that time, too, I named among the dyes which can be used for orthochromatic photography: eosin, methyl violet, erythrosine, cyanine and others. The following passage in the addendum to the minutes of the meeting proves that the orthochromatic reproductions I presented at the festive meeting on September 10th in Frankfurt were also successful from a practical photographic point of view (Photographische Correspondenz, 1884, pag. SE whose color combination is very unfavorable for the usual process and shows the photograph produced in this way so different effects that it cannot even serve as a copy of the original; a second, produced according to the new method, agrees completely match the color effects of the original.

A second picture, "Landscape" by Hildebrand, speaks even more strikingly in favor of Dr. Eder (sunset, red-yellow clouds in the blue sky). The effect of the painting is that the yellow clouds emerge brightly from the darker evening sky. In ordinary photography the opposite is true, in that one believes black thunderclouds are rising in the bright sky

to see rise. The orthochromatic image, however, corresponds completely to the effect of the original.

With other pictures, such as a "landscape" with figures by Boehm, a "vegetable

trader »(watercolor) and so on, does the speaker know how to prove the correctness of his theory in the most glaring fashion? >

!) To avoid misunderstandings, I note that the term "iodosine" means the same as "erythrosine" and both names were chosen by different tar paint factories to denote the same product, which is common in the paint industry happens.

?) "Erythrosine yellowish" consists mainly of

bromeosine. s0 JeN. bidet

I presented the results of my work with erythrosine and the other sensitizing dyes examined by me at that time to everyone who was interested in them, including Mr. Ch. Scolik, who in 1884 after the appearance of Prof. Vogel's azaline plates Experiments (at that time still in Kroh's studio in Piaristengasse) and made an announcement at the plenary meeting of the Vienna Photographic Society on October 7, 1884).

At the same time, Mr. Scolik wanted to try color sensitizers himself and visited me in the chemical laboratory of the old k. k. Staatsgewerbeschule in Vienna (at that time still in the 1st district, Annagasse), which I chaired at the time and where I carried out my photochemical experiments; At his request for a sample of the eosin which I had recommended in the above-mentioned papers, I gave Mr. Scolik a sample of Schuchardt's "bluish eosin" (erythrosin). Since the quantity of this dye available to me was very small and I could only give off a small remainder of the erythrosine, I informed them that this dye had been obtained from Schuchardt in Görlitz and advised Mr. Scolik to do the same. This "bluish eosin" (that is erythrosin) started the production of color-sensitive plates. The correctness of this presentation emerges from the frank and frank communication of Mr. Scolik himself. In the first essay that Mr. Scolik wrote on 'color-sensitive processes' and published in the Photographische Correspondenz of 1884, p. 319, it says literally: 'I used orthochromatic plates for comparative experiments with self-made plates preferably cyanin and eosin (bluish), because according to the instructions of Prof. Dr. Eder and the important work of Schumann?) It was precisely these that appeared to be the most noteworthy'.

From this it is clear that I not only used erythrosine as a sensitizer for the first time, but also expressed its advantages as a sensitizer for yellow and green and suggested that other experimenters should continue to try the erythrosine. I also described in my treatise: "On the behavior of the haloid compounds of silver against the solar spectrum and the increase in their sensitivity to dyes" (cf. pag. 1 ff. Of these treatises), which was published on December 4, 1884 of the Imperial Academy of Sciences

presented in Vienna and published in its meeting reports, the spectroscopic behavior of the "bluisheosin".

I believed that I had done enough to introduce erythrosine into orthochromatic photography, all the more since Mr. Scolik later worked with Dr. Mallmann met for joint experiments on orthochromatic plates and both of them stated in their lecture on February 16, 1886 that they would continue to build on my findings. In this lecture, which is printed in the Photographische Correspondenz, 1886, p. 135, it says: "In the specialist literature there are some brief statements about the dyes of the eosin group, used as a bath; these are partly from Prof. Eder, who in 1884 gave the Photographic Correspondence a special bath recipe for erythrosine ammonia, which, however, prescribes the dye solution in a concentration which reduces total sensitivity. Eder's statement in his Academy paper of December 4, 1884, his statements in this regard that of the dyes he investigated, he generally stated that 2-4 mg were dissolved in 100 g of water, 2 5 minutes to bathe and possibly to increase the dye content. At the same time he mentions

the favorable properties of ammonia in terms of yellow sensitization ».

1) Photographische Correspondenz, 1884, p. 290 and 319. 2) Schumann had especially recommended cyanine.

On the history of orthochromatic photography with erythrosine. 81

Following this, Mr. Scolik and Dr. Mallmann, according to Schumann's instructions, to bathe the silver-bromide gelatine plates first in dilute ammonia and only then in weak ammonia cal erythrosine solution.

At the end of his "Contributions to the Knowledge of the Silver Compounds of Eosins" ("Photographische Correspondenz", 1889, p. 122), Prof. Emil Zettnow added a historical note about erythrosin, in which he said: "The first We owe the use of erythrosine as a sensitizer to Prof. Eder (1884); after him, Mallmann and Scolik were particularly concerned with it in February 1886 and inspired by it, and soon a large number of researchers".

To this day I have had no reason to comment on this, as the facts just described show that I can fully claim the priority of the discovery of erythrosine as an excellent sensitizer for yellow and green, and so can Mr. Scolik was made aware of this dye, which is so important for orthochromatic photography, by me.

The reason for this historical description was rather a passage in the work: "Die orthoskiagraphische Photographie" by k. and k. First lieutenant Ludwig David and Charles Scolik (published by W. Knapp in Halle a. S., 1890), where the authors write on p. were carried out in the photochemical test laboratory of Dr. F. Mallmann and Charles Scolik ... Among other things, the merits of erythrosine were first pointed out there and this was generally introduced into practice through the experiments carried out with it.

The authors refer to the above-cited paper by Prof. Zettnow's in the "Photographische Correspondenz", 1889.

I would like to point out the following: If Prof. Zettnow, to whom Lieutenant First Lieutenant David and Ch. Scolik cited, had written this in the cited passage, I would have immediately protested. However, according to the previously quoted wording in Prof. Zettnow's paper, this is not the case, but the same acknowledges my undoubted priority claims about the introduction of erythrosine as a sensitizer for orthochromatic bromosilver gelatine plates; In fact, it was I who first pointed out the benefits of erythrosine and not Dr. Mallmann and Mr. Scolik. In fact, neither Dr. Mallmann, nor Mr. Scolik raised in their treatises, and Mr. Scolik himself published (as previously mentioned) the fact that he used "eosin bluish" (that is erythrosin) because this, according to him my instructions, as well as cyanine, appeared to be the most noteworthy dyes after the work of Mr. Schumann.

I myself value historical accuracy. Not everyone is interested in the history of inventions, and the practitioner takes the good where he can find it without asking who it comes from. I don't want to fight against that here; but if, in historical accounts, older priority claims are overlooked, which is easily possible, I consider it necessary to pay attention to this. This is why, in order to maintain my priority of discovering the excellent properties of erythrosine as a sensitizer to silver bromide gelatin, I penned up and reminded them that I should look at the benefits of erythrosine first.

pointed

out.11

About purification of the sensitizing

cyanine.Of

JM. Baths:

The cyanine is a good sensitizer for orange and red. All cyanine on the market is so-called iodine cyanine.

Occasionally, some commercial grades, not all, or perhaps some types of emulsions that have been colored with cyanine, develop a haze during the induction.

If such cyanine is treated with hydrochloric acid, the tendency to form fog is reduced ("Photographische Correspondenz", 1891, p. 313). This treatment can easily be done in the following way: You powder the cyanine and pour something over it in a porcelain or platinum dish. Water and hydrochloric acid. With frequent stirring, you evaporate to dryness in a water bath, moisten the residue recently with hydrochloric acid and evaporate it again in a water bath. A residue remains which still contains traces of hydrochloric acid and is therefore not completely blue. If you carefully warm the bowl in a sand bath or over a wire mesh until the edges of the cyanine layer are dark (shiny metal), the last residue of hydrochloric acid escapes. Incidentally, even a small trace of hydrochloric acid does little harm because the cyanine is usually mixed with ammonia for sensitization and the hydrochloric acid is neutralized in the process.

As Dr. E. König showed ("Jahrbuch für Photographie", 1903, pag. 9) that the iodine content of the cyanine remains unchanged

so that it is not a matter of decomposing the cyanogen iodine into cyanogen chloride, but rather a purification of impure dyes.

!) Cyanine discolors with acids and turns blue again with alkalis.

Spectrographic experiments with silver bromide  
collodion. Of

Dr. A. Jonas.

From: "Orthochromatic bromosilver collodion emulsion" (Photographische Correspondenz,  
1891, pag.BUS):

To test the color sensitivity of emulsions to the solar spectrum, asked  
Director Eder and I did a few experiments with the glass spectrograph  
at = E

Sensitometer samples with Warnerke's sensitometer and the amyl acetate lamp from Hefner-  
Alteneck as the light source.

EEE EEE BEEEEEEETEROCTELTEETCHEE SEEN SEE  
SUEEFSECEE TEENS  
SERIEAEGERFGEEBTRSFEREFENEZUSTRERRERNEIUTE  
BLOCK]

Tr u

|| 'Exposure Degree Be Dyes Distance] Em- | a | Warnerke | â € œAndleness | | Wet Collodion  
method. . - 25 cm | 1 minute 9 | 1 silver oxide ammonia - bromide silver | eollodion emulsion  
227 2% -

25 cm || F 6) Sn 3 eosin silver Im 1 E 17 150 R with silver excess l m 1 & 20â€ 21 | 350â€ 400 & erythrosine silver l m 1 s 14â€ 10 790 â€ % a with excess silver Im | 1 n 2 400 5 Phloxin silver 1 m! 2

17 150 r Rose bengal silver 1 m 1 E 15 90 5 cyanine erythrosine silver | In the | 1 R 12 â€ 18 40 â€ 50 r cyanine Zosend a] 2 10) {Silver oxide ammonia - bromosilver collodion emulsion, bathed in SI Ä ± oer Tananlosune 2 - Zaren x 5 Be Dr. E. Albert's Collodione emulsion - 25 cm || A 9 {5e dye P of Im 1 5 20â€ 21 | 350-400 Dr Be Albert

1) The large Steinheil Spectrograph with three glass prisms was used. 2)

very slack, 84 Dr. A. Jonas, Spectrographic Experiments with Bromsilber-Collodion.

First, the uncolored Collodione emulsion was tried and the usual sensitivity curve found (see Eder's "Detailed Handbook of Photography", Vol. I, p. 242). The addition of the silver compounds of the eosin pigments causes a huge maximum between E and D in green and yellow, which is much more important than the maximum in blue. The relatively greatest sensitivity in the yellow-green is given by eosin and erythrosin; There is little difference in the behavior of the two, except that the sensitization maximum of the latter is a little further towards the less breakable end (analogous to the behavior of bromosilver gelatine erythrosine plates).

In the case of phloxin and even more strikingly in the case of rose bengal, the maximum sensitization is a little further towards orange, but the overall sensitivity of the emulsion dyed with it is lower and so is the relative yellow-green sensitivity. That is why the usual eosin or erythrosin was ultimately chosen, since these are easiest to obtain in a chemically pure state. The spectrum of the eosin collodion is, however, not identical to that of Albert's emulsion, in that the latter shows a weak sensitization maximum at D! /, C in addition to the strong maximum in green and yellow-green (between E and D, which belongs to all eosin colors) . Otherwise the general character of the sensitization and the behavior of the emulsion in the photography of color plates is very similar.

The addition of picric acid ammonia reduces the sensitivity of the eosin emulsion to blue and violet in a very noticeable way. The spectrum on a bromosilver collodione emulsion mixed with eosin silver and picric acid ammonium shows a weak effect in violet and blue, which is followed by the enormous maximum of sensitization in green and yellow without any noticeable interruption. With a very short exposure in the spectrograph, only the latter maximum appears.

Cyanine makes the emulsion sensitive to orange. a weak effect extends through red into the infrared.

Eosin silver and cyanin give two sensitization maxima, but spots easily develop in the layer and the overall sensitivity suffers, so that this mixture has not proven itself as a sensitizer for the reproduction of colored objects for the time being. On the other hand, eosin and erythrosine, together with picric acid ammonium, do excellent services.



In the original paper cited, the following are dealt with in detail: silver oxide ammonia bromosilver collodion emulsion; Coloring of the emulsion; Effect of excess silver oxide ammonia in the colored Collodion emulsion; en method with the Collodion emulsion; Raw emulsion; Eosin silver solution; Erythrosine silver solution; Treatment of glass plates; Preparation of the plates; Choice of the Denkellamteaeriee! Exposure and evocation of the panels; Concentrated hydroquinone evocation ;; Veinbefore fixation; Reinforcement after fixation; Weakening.

New sensitizers for silver bromide  
gelatine.Of

J. M. Eder and E. Valenta.

(Photographic correspondence, 1894, p. 227.)

I. Rose bengal varieties. Of the recent years n

We have received about a hundred different samples from the dyes produced by the kindness of the gentlemen manufacturers and patent holders. Of these, we particularly included the new eosin derivatives in the circle of our investigations, because we had bluish rose bengal varieties from both the Badische Anilin- und Sodafabrik, as well as from H. Grothe in Basel, whose effect extends further against orange than this was the case with the earlier varieties. The best behavior was tetraiodotetrachlorofluorescein, whose sensitizing effect for silver bromide gelatine plates in the usual concentration!) Rises to a maximum in green-yellow in front of the Fraunhofer line D and shows a clear sensitizing effect up to D! /, C . This sensitizer is therefore the most sensitive to orange-yellow of the well-known rose bengale varieties. Since the sensitization curves of this dye have already been reported by Dr. E. Vogel in his inaugural dissertation: "About the position of the absorption strips and the light sensitivity of organic dyes" (1890) and these are analogous to those of Rose Bengale (only that they extend further towards orange), THAT is how it appears to us Superfluous to add Curven especially via the dye. We recommend the use of this dye for the production of orthochromatic bromosilver gelatine plates if a greater sensitivity to orange is to be achieved with the use of yellow discs. The overall sensitivity of the plates stained with it is noticeably inferior to that of erythrosine plates.

2. Rhodamine dyes. The common commercial rhodamine is closely related to the eosins. It is a dye that is soluble in water with a bluish-red color, the fluorescent solution of which makes the yellow- green bromide-silver gelatine plates between E and D sensitive. This sensitizer was first studied by J. Waterhouse, then by BothamleyÂ °).

However, since the effect of this dye is far inferior to that of erythrosine, it deserves no further consideration for the production of orthochromatic plates. It is different with the new ones

Types of rhodamine, which chemically differ significantly from rhodamine.

1) 1 g of dye dissolved in 500 parts of water, 1 cm<sup>2</sup> on 100 cm<sup>2</sup> diluted, mixed with 1 Å ° /, ammonia, used for bathing the plates. 2?) Eder: "Yearbook for Photography and Reproduction Technology", 1890, pag. 309 and 1891, pag. 423,

86 JaM = RdeÄ ± sundB, VNalental

The common rhodamines are namely according to the D. R. P. 71490 (of March 11, 1892) the Baden aniline and soda factories to be regarded as acids, which the formula

& RA, NR,

O TEHNRGO

UCâ € "6, (2) H, â €" COOH, in which formula R denotes methyl and ethyl. By treating them with mineral acids, new dyes with a more bluish tinge are created, "ethylated rhodamines", which act as esters

consider are whose constitution of the

formulaC, H, NR,

2 eEaNB

> = UCâ € "(, () H, â €" COOR corresponds (Chemisches Centralblatt, 1894, pag. 128).

The dyes of the last-named series come after the reports from the Badische aniline and soda factories in Ludwigshafen a Rh. On the market as Rhodamine 3B, however, in a weakened form. The pure preparation is tetraethylrhodaminaethylester (hydrochloric acid salt). We received a sample of it through the kindness of the management of the factories mentioned.

The "Basel Society for Chemical Industry" was also kind enough to send us a sample of this dye along with other dyes. Rhodamine 3B dissolves in water with a violet-red color and a magnificent orange-red fluorescence. Do you add to 100 cm<sup>2</sup> Water 1 Å € "2 cm<sup>2</sup> Rhodamine solution 1: 500 and 1 Å ° /, ammonia, this is how the silver bromide gelatine plates bathed with it become | very sensitive to greenish yellow, yellow and orange; the maximum of the sensitizing effect is E Å ° /, D and extends to DJ, C; the orange sensitivity of these plates is broadly similar to the rose bengale plates mentioned earlier, but is slightly greater.

We believe that rhodamine 3B is one of the good, practically useful sensitizers. The cheapest dyes of the rhodamine series, which we have investigated so far, are two violet-red (strongly bluish) types of rhodamine:

- a) the tetrachlorotetraethyl-rhodamine-chlorohydrate, which was kindly sent to us by Mr. I. Schmid, Director of the "Society for the Chemical Industry in Basel" (aniline paint factory). This dye causes a strong sensitization for green, yellow and orange; the sensitization maximum begins before D in yellow-green and extends to orange-red (D! /, C to DJ, C). The sensitization maximum for tetrachlorotetraethyl rhodamine methyl ether extends even further towards orange. This dye

causes a small maximum of sensitization in green between E and D; the second, stronger maximum begins in yellow-green before D (D 270 to D \* /, C). It should be noted that the hydrochloric acid diphenylrhodamine and the diphenylsulfonic acid soda are poor sensitizers in contrast to the above-mentioned rhodamine derivatives;

b) a very bluish-tinged preparation manufactured by the Badische Anilin- und Sodafabrik, which the named factory calls Nitrilo-Rhodamine. This dye, which also fluoresces very nicely, shows both the absorption band and the sensitization maximum moved further towards Roth. The orange sensitivity extends to D \* /, C into orange-red; Exposed behind a copper ruby disk in the solar spectrum, Fraunhofer lines B and C can be photographed with ease with both the chlorinated rhodamines mentioned above and with nitrilo-rhodamine and even traces of A. The relative blue sensitivity is but larger than erythrosine or rose bengal. |

The sensitivity to orange-red is not so great in the rhodamine colors as in cyanine, the sensitization maximum of which extends further towards the red end of the spectrum; on the other hand, the rhodamine dye mentioned has the great advantage over cyanine, which is generally

New sensitizers for silver bromide gelatine. 87

The ability of the silver bromide gelatin plates to not depress significantly, which is the case with cyanine to a large extent. The rhodamine dyes mentioned, in particular the tetrachlorotetra- aethylrhodamine-methyl ether and the nitrilo-rhodamine, are important for orthochromatic photography that should not be underestimated, because red pigment colors can be photographed quite well with such plates using an appropriate yellow disc, without having to unduly increase the exposure time. We have also successfully used this dye for the purposes of spectrum photography, namely for photos in the area of the Fraunhofer line D. The spectral lines are more sharply expressed than is usually the case with cyanine plates

3, acridine dyes. These dyes include some that have a pronounced sensitizing power, for example chrysaniline; The acridine yellow and acridine orange behave better than this, causing a sensitization of bromide silver plates all over the green up to the vicinity of D, and even a little above that with stronger exposures.

The most favorable is the acridine yellow, which was kindly made available to us by the A. Leonhard company in M<sup>1</sup>/<sub>4</sub>hlheim (Hesse). The dye is the Chlorhszdrar.des Diam<sup>±</sup> do- Dimethylacridins; it is heavy in water, more easily soluble in hot alcohol with its own carbide and intensely green fluorescence.

Saturated aqueous solutions must be used for sensitization, or, better still, saturated alcoholic solutions must be diluted with equal parts of water. These solutions are used to bathe the plates without the addition of ammonia. Acridine yellow-bromide-silver gelatine plates show the most favorable green sensitivity that we have come across so far, in that when photographing the spectrum (in the solar spectrograph) a closed band from D1 /, E to violet appears. For this reason the acridine yellow will be useful not only for spectral photography but also for the purposes of polychrome photographic printing. (Unfortunately the gelatin layer is colored quite strongly yellow by this dye.)

With regard to the absorption spectra and the sensitization maxima caused by them on silver bromide, all of the sensitizers described here have the known relationship that

means that the sensitizations obey the law of absorption. Mode of action of sensitizers in orthochromatic processes.

Of  
J. M. Eder.

(Photographic correspondence, 1894, p. 457.)

It has now been 10 years since I began my spectrographic investigations into the mode of action of the "optical sensitizers" discovered by Prof. H. W. Vogel and created a very comprehensive experimental observation material, on the basis of which I mean Developed views on the theory of the sensitizers (see pag. 10 and ff. Of these treatises).  
I. Coloring of the bromide silver by molecular attraction.

The first requirement I made on those dyes that are supposed to have a sensitizing effect on silver halide salts was:

"The dyes must color the grain of silver bromide". Furthermore: "The dyes that strongly sensitize are also all so-called substantive dyes", that is, they color the substances directly, probably through molecular attraction.

Then I developed my theory of sensitizers based on molecular vibration of the colored molecules and made them the subject of the celebratory speech occasionally at the Daguerre celebration of the Vienna Photographic Society on October 15, 1889 (see p. 75 and following of these treatises).

The above-mentioned requirement for a sensitizing dye had never before been scientifically specified, but the main emphasis was placed on the fact that the dye should chemically bind bromine or - if it does not have this property - some another "chemical sensitizer" (bromine absorber) was present. The beneficial effect of chemical sensitizers in the orthochromatic process is recognized, but it is not enough to turn a dye into a sensitizer; instead, according to my point of view, a dye must primarily color the grain of silver bromide, the bromosilver molecule itself, in order for it to be used for photography Effect to arrive.

That this theory is related to practice emerges from the later investigations of other researchers; In particular, Baron Huebl's more recent experimental investigations (see Eder's Jahrbuch für Photographie und Reproduktionstechnik, 1894) yielded results which gave brilliant confirmation of the views I expressed in 1884.

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Mr. Baron Huebl occasionally found in his studies "On the behavior of bromine silver to colorants" that bromine silver, which has been precipitated on the one hand with excess soluble bromide and on the other with excess silver nitrate and then washed, behaves differently towards eosin It; the former is neither colored nor sensitized by eosin, while the latter is the opposite. He observed something similar in quinoline red and cyanine. Furthermore, Baron Huebl observed, for example, with cyanine, that the only important thing is that the bromide silver must be made susceptible to the staining by cyanine by suitable preparation (presence of a trace of silver nitrate); then the cyanine acts as a color sensitizer, but otherwise it is ineffective, even if chemical sensitizers (narcotine etc.) are added. Mr. Baron Huebl draws the following conclusions: "In order for a dye to act as a sensitizer, it must color the grain of silver bromide, or at least be in close, firm contact with the silver bromide; the presence of the same in the still moist binder is not sufficient. The connection of the dyes with the bromide silver should in most cases be traced back to molecular attraction ".

For comparison, I put the wording of the views I expressed in 1884 next to it: "According to the (own) observations I have made so far, the dyes sensitizing to silver halide salts must meet the following requirements: 1. They must color the bromide silver ... the silver bromide combines with the dye through molecular attraction 2. You must show an intense band in the absorption spectrum".

This is a complete confirmation of my theory.

#### II. Favorable influence of silver chlorine in orthochromatic processes.

My investigations into the influence of the presence of chlorine silver on the sensitizing effect of dyes date from the year 1884. In the plenary meeting of the Viennese Photographic Society on May 6, 1884 (Photographische Correspondenz, 1884, pag. 143) I stated: "The experiments with chlorosilver, chloriodine and chlorobromosilver gelatin emulsions showed that they can be made relatively more sensitive to yellow and yellow-green than silver bromine as soon as a suitable coloring agent (e.g. eosin) is added. The sensitivity to yellow can thereby be increased enormously Under these circumstances, the chlorine, chloro iodine and chlorobromide silver

in the form of gelatine emulsion is superior to the bromine silver gelatine in terms of the relative sensitivity to yellow. By studying the behavior of chlorobromosilver against color sensitizers in the case of Collodion emulsions, Herr Baron Huebl found, for example, cyanine in such mixtures to be much more powerful and more reliable than with bromosilver alone; on this he founded a very effective method for the production of orange-sensitive collodion plates (Hübl: "Die Collodionemulsion", 1894) and on this occasion he mentions my earlier analogous investigations with gelatine emulsions.

This essential extension of our knowledge of Collodion emulsions by Mr. Baron Huebl, which is very important in practice, generalizes my observations, which were initially only made with gelatine emulsions, about the increase in the sensitizing effects of dyes by adding them

from chlorine silver to bromine silver emulsion.

#### IH. About the action of gelatin as a chemical sensitizer for

Silver bromide and its repercussions on the sensitizing effects of dyes.

It is to the great merit of Prof. H. W. Vogel's to have shown that bromide silver in shape of gelatin emulsion shows a different spectral behavior than the bromosilver collodion-1290 J22MssEider.

emulsion. The former has the maximum sensitivity in light blue, the latter in indigo blue. After this difference had been established, it was believed that the different overall sensitivity of both types of emulsions to white light could be explained exclusively by the two types of "modifications of bromide silver". The question of whether gelatin could act as a chemical sensitizer here was not raised at the time. When I carried out my investigations into the theory and practice of the silver bromine gelatine emulsion in 1879 and 1880 and published it partly in the Photographische Correspondenz, partly as an independent work (the first independent book on silver bromide gelatine to be published in German), I pointed out that gelatin is a chemical sensitizer in the strictest sense of the word. This view was later generally accepted. A completely new confirmation of the same results from the groundbreaking studies on ultraviolet-sensitive silver bromide published in 1893 by Mr. V. Schumann in Leipzig. Although Mr. Schumann embarked on a completely new path in the manufacture of bromide silver plates, he nonetheless came to the conclusion that gelatine acts as a chemical sensitizer in the case of bromide silver (meeting reports of the Imperial Academy of Sciences in Vienna, 1893).

So let us stick to this assumption and then ask the following question: "Does gelatin as such also play a role in the bromide-silver emulsion process with regard to color sensitization through dyes?"

This question is justified because it has long been known that bromosilver collodion, on the one hand, and bromosilver gelatine, on the other, do not behave in the same way towards sensitizing dyes. |

Let's take a closer look at an example with a carefully examined sensitizer, cyanine, the properties of which for collodion emulsion were studied in great detail by Baron Hübl in 1894!), While I myself worked out exactly how this dye works for gelatine emulsions at the time have examined. If you use cyanine (that is iodeyanine) or, better, chloreyanine 2) to sensitize bromidesilver, the result is: |

1. Bromosilver collodion, prepared and washed with excess, soluble bromide, is not stained by cyanine, but is also not sensitized, even if a chemical sensitizer, for example narcotine, is present(Hüb)).

2. Silver bromide gelatine, produced in an analogous manner using excess soluble bromide, is however strongly sensitized by cyanine and the grain of the silver bromide is also colored.

It follows from this that in this case the better effect of color sensitization by cyanine is not due to the gelatine due to its property as a chemical sensitizer, but most likely the gelatine only acts as a stain for the dye mentioned. Since I discovered as early as 1884 that the bromosilver molecule in photographic emulsions stubbornly adheres to gelatine and that the latter adheres closely to the former, as soon as the conditions for the usual emulsion preparation are adhered to, this assumption becomes more probable . In my opinion, these would be intermolecular processes, which can be traced back to multiple molecular attractions of the bromide silver, whereby the gelatine plays a mediating role in the sense of the dyer's stain. =

The case described is one of the few cases in which the silver bromide gelatin plate can be better sensitized than the bromosilver collodion plate: however, this is only an exceptional case,

) Eder: "Yearbook for Photography and Reproduction Technology", 1884, pag. 189; also Hübl: "Collodionemulsion", 1894 (Halle a. d. S.). :

?) First examined by me and recommended (including details of the mode of presentation) in 1891 (Photographische Correspondenz, 1891, pag. 311) for gelatine emulsion. Baron Hübl recently confirmed the good properties of chloreyanine compared to common cyanine with Collodionemulsion (Hübl: "Collodionemulsion", 1894).

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because the sensitizing effect of dyes is usually clearer and stronger with bromide-silvercollodion than with gelatine emulsion.

The reason for the latter usually occurring et: kei, is probably that on a pure gelatin layer the dyes are much more powerful than on Collodion's skin, which seldom really turns color, but from which the dye is mostly

is very easy to wash off. It is not only the grain of the silver bromide that is colored in the silver- bromide gelatine plate, but also, presumably, to a much greater extent, the rich gelatine layer with the coloring agent. These gelatin masses, which are stored next to and in front of the grain of silver bromide, are more or less strongly colored, and have no direct effect on the sensitization of the silver bromide, but rather disturbing; because these colored foreign layers

act as absorbing screens (which Prof. H. W. Vogel already points out) and reduce the sensitivity to light. These secondary dye effects interfere with the sensitizing effects of the dyes in the bromide silver and would be seek as much as possible to belittle.

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Notes on orthochromatic recordings and the method of spectrographic examination. Of

J. M. Eder.

(Photographic correspondence, 1895, p. 545.)

In No. 421 of the Photographische Correspondenz, 1895, p. 494 there is an article by Fred. E. Ives "About orthochromatic recordings with ordinary plates", which gave remarkable hints about color filters and the use of chrysoid and naphthol yellow etc. for this purpose, which agree with my experiences. In this article, however, Ives expresses several general principles which encroach on the field of spectrum photography and with regard to this I cannot agree with him, but consider a clarification of the same to be necessary. | |

Ives constructed a spectrograph with "a set of lightweight crown glass prisms" and experimented with different types of plates and came to several conclusions, which I will discuss here.

Ives says (p. 498): "The relative effect in dark violet or ultraviolet is much stronger in ordinary photography than is generally assumed". This "than is commonly believed" view expresses a subjective opinion that Ives apparently had in mind when saying it. But this does not apply to us, because we have repeatedly described the effect of the colored rays of light and depicted them in photograms and pointed out the enormous relative effect of the more strongly breakable rays, which is only greatly reduced when certain types of glass are used. The relatively photographic effect of the violet and ultraviolet is evident from the comparative experiments with glass and quartz spectrographs, which have also passed into the photographic specialist literature (see Eder and Valenta's treatises, Photographische Correspondenz, 1894, p. 386), at least generally known in German literature.

Furthermore, Mr. Ives could not reconcile the results of his spectrographic examinations with his photographic recordings and concludes from this that "spectrographic examinations, as they are usually done, are not competent to determine the photographic value". I have no objection to this view, provided that what is meant by it is that spectrographic tests are usually only done very superficially; in the latter case they are of course not competent. But will the spectrographic work

If done correctly, the conclusion on color sensitivity etc. is completely competent. Comments on orthochromatic recordings etc. 093

For spectrographic work you have to take into account the nature of the spectrograph (glass, quartz, grating), then you will find a correct use for the test results depending on the nature of the spectrograph.

One must be careful not to accept Ives's view "that crown glass prisms do not even remotely indicate the true photographic value of the more refractive rays" "as generally accepted. Crown glass prisms indicate the true photographic value of the more powerfully breakable rays, of course, with reference to the absorption of this type of glass against light. If one wants to avoid

this influence, the spectroscopist has to work with quartz or with concave gratings!), With which the work is of course more difficult. The photochemist just has to take into account the absorption ratios of the optical apparatus in order to be able to draw correct conclusions; if the circumstances are not observed, the best spectrograph gives wrong results.

With the correct work process and correct interpretation of the test results one will no longer find it "strange" that spectroscopes & vision directe show "no effect in the ultraviolet", because it has long been known that the thick glass masses are more of this kind Prisms totally shift the curve of the color sensitivity and naturally also have to shift it, since the absorption of the short- wave rays here is a very large one; that the Jenenser

We have already demonstrated that glasses behave very differently and one must also be careful not to draw up general sentences on the basis of individual observation.

In addition, the photographic objectives themselves have different color permeability for the violet end of the spectrum; For example, the triple cemented double anastigmat absorbs much more violet and ultraviolet than is the case with thin, single or double cemented lenses made of more permeable material.

In spectrographic work and inferences about orthochromatic photography, one has to consider not only the nature of the optical apparatus, but also the brightness distribution of the colors in the spectrum of direct sunlight, on the one hand, and, on the other hand, the colored natural object to be photographed, which sends reflected light into the apparatus, take into account. In the spectrum of direct sunlight the brightness of the red and yellow rays appears to be distributed quite differently than when one examines the reflected light of a street picture; It is therefore by no means surprising when, for example, when taking a spectrum photograph behind chrysoid filters, Mr. Ives seemed to maintain "40 ° /, the overall brightness at the red end", but when taking a "street picture" had to expose eight times longer to naphthol yellow. These phenomena are easy to explain with the help of spectroscopy in the above sense and all these apparent contradictions are resolved by the correct application and interpretation of spectroscopy.

In his article, Mr. Ives also discusses the question of whether ordinary plates behind colored light filters can do the same thing as orthochromatic ones. This question has long been decided in favor of the orthochromatic plate through innumerable experiments. However, there may be cases in which the ordinary plate can provide a truer color shade value than the orthochromatic plate, for example in the reproduction of very colored objects in which red, green and blue of approximately the same optical brightness values occur, but contrast strongly due to their different color. If one reproduces such objects with ortho-  
chromatically completely correct brightness values, the color tones must consequently be in the

1) Such spectrographs are available at the k. k. Graphic teaching and research institute (except for the glass spectrograph) also in use.

94 J. M. Eder, remarks on orthochromatic recordings, etc.

Reproduction flow together. You then either have to emphasize the red at the expense of the blue by adding darker yellow discs or you take the opposite path, that is,

one uses lighter panes and little or no orthochromatic plates. Then | separates the drawing of the colored objects again in clear contrasts. However, these apparent anomalies do not in fact contradict the theory. Be



Furthermore, one must not forget the long-known fact that the usual bromosilver gelatine plates have the maximum sensitivity in blue and violet, but are also noticeably a little sensitive to green and yellow, and even to red; Spectrum photography also proves this. If Ives now uses this very weak red, yellow and green sensitivity to photograph colored objects behind colored light filters in very bright light and with very long exposures, he may very well have obtained a negative under favorable circumstances; Of course, the red and yellow pigments (insofar as they do not have a blue-green effect) have a weak effect, but perhaps a flattening, a lowering of the contrasts of the glaring image effect is desired, because, as mentioned, such feet can be used Here and there the character of the reproduction come to be equipped. However, if you use plates in which the above-mentioned residues of sensitivity to red, yellow and green are missing, as is the case, for example, with wet iodized silver collodion plates, then the lack of a color sensitizer will be so palpable that you will in spite of it the yellow disc as a color filter will not achieve a color-correct image if the experiment is carried out correctly; But if you choose color filters that are not impermeable to blue and blue-green, such rays naturally creep into the photographic camera and cloud the test result. |

Strong red, yellow and green effects in photographic recordings can only be achieved - with or without the use of color filters - if the plate has been sensitized to these rays by suitable dyes or, as is known, Similarly says when using orthochromatic plates w earth.

The enormous benefit of the orthochromatic method is so well known to the reproduction establishments, whose specialty is painting reproduction and art publishing, that it would mean bringing owls to Athens to emphasize it. On the other hand, it is just as indubitable that modern orthochromatic photography, both theoretically and practically, was created and scientifically justified with the help of spectrum photography. Taking a spectrum photograph is not difficult; The correct interpretation of the results and the establishment of the connection between the test results with reference to the variable light absorption of the photographic apparatus, the spectral composition of the incident and reflecting daylight (the lighting), the color filters and the sensitivity of the orthochromatic plates is far more difficult. Such questions require thorough physical comparisons of the kind mentioned, and if the spectrograph comes into an apparent contradiction with the photographic reproduction of a chromolithography, then the apparatus in and of itself cannot be described as unreliable, but has become interprets the test results poorly.

The spectrograph remains the most indispensable analyst of all color phenomena, without its purposeful application a deeper penetration into the world of colors and into the photographicchemical phenomena is unthinkable.

The different methods of sensitizing gelatin emulsion plates by bathing in cyanine solutions.Of

Hugo Hinterberger.

(Photographic correspondence, 1896, p. 131.)

The best known and most commonly used sensitizer for Roth is cyanine, an intense blue dyemade from quinoline (C, H, N))).

Dr. V. Schumann, to whom we also owe extensive work on the coloring of the emulsion. The same recommends a 100 cm pre-bath? Water and 0'25â € "2 cm? Ammonia (0'936) to apply,

after which the plate in a sensitizing solution of 100 cm<sup>3</sup> Water, 1 cm<sup>3</sup> Ammonia, 5 cm<sup>3</sup> 10% alcohol, 2

When using this recipe, I always get more or less impure and veiled negatives  
5 cm<sup>3</sup> alcoholic cyanine solution (1: 500) should be bathed for 2 to 4 minutes.  
There

I tried the Weissenberger \*) method and achieved far better results, particularly with regard to the clarity of the plates. The same uses a cyanine solution slightly acidified with acetic acid and thus discolored, without using a pre-bath?). The color returns during the drying of the plate after the acetic acid has evaporated and causes a strong sensitization of the silver bromide grain for a rather narrow spectral region between C and D in orange, while the sensitivity for blue and violet between F and A is pressed. In order to determine both the limits of the effectiveness of cyanine in acidified solutions as well as the most beneficial amount of it, I prepared mixtures which contain very different amounts of cyanine and those from the table on pag. 96 can be seen.

1) H. W. Vogel: "The Photography of Colored Objects", p. 116.

2) Even in hot alcohol I did not get a complete solution of cyanine in the ratio 1: 500; For the sake of simplicity I nevertheless used alcoholic, filtered solutions prepared in this ratio for my experiments.

3) Eder's "Detailed Handbook of Photography", Vol. III, p. 159.

+) Photographic Correspondenz, 1886, p. 591.

5) 100 cm<sup>3</sup> Color bath contain approximately 2 cm<sup>3</sup> my cyanine stock solution (1: 500).

6) The baths were made by first acidifying the distilled water and then adding the appropriate amount of alcoholic cyanine solution while stirring.

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Solution II incidentally corresponds to Weissenberger's recipe, while solution II /, Times, solution III contains 10 times and solution IV 100 times as much cyanine. The effect of the four baths on ordinary silver bromide gelatine plates (Schleussner plates) can be seen from Table III, which shows the spectrum of the brightly shining flame of the luminous gas (a Siemens burner was used). The letters designate the regions corresponding to the solar spectrum, respectively the position of the Fraunhofer's lines in the solar spectrum in relation to the cyanine's active strips. The recordings

ee Alcoholic Concentrates

see a cyanine solution 1: 500 acetic acid

I 100 cm<sup>3</sup> 0.01 cm<sup>3</sup>) 1 drop 1,175 100 cm<sup>3</sup> O2 em) 1 A III 100 cm<sup>3</sup> 10 centimeters?

1 A IV 100cm<sup>3</sup> O0: em 1 i

were produced by means of Steinheil's small spectrograph, after which the plates were put together in pyrosoda developer with 10 drops of potassium bromide (1:10) for 5 minutes in almost complete darkness

have been developed for a long time. The copying of these four plates and a plate (No. I) prepared according to Debenham's method and exposed under the same conditions was carried out in a copying frame. There are four different exposures on each plate for the purpose of measuring sensitivity (15, 30, 60, 120 s); for reproduction the Speeltar produced with exposure for 2 minutes were used:

Addition of quinoline red in acidified cyanine baths.

A color effect very similar to that according to Debenham's recipe is achieved by using a mixture of cyanine and quinoline red, as was first used by Vogel to depict his "azaline plates" in 1884).

Mixtures of cyanine and quinoline red can also be used in acidified solutions, and in order to test the influence of the latter - added in different amounts to the dye bath - on the color sensitivity of the plates bathed in the same, I have the following B&A order in connection with Reece Net. tries:

Distilled    Alcoholic    Concentrated

Alcoholicw Ka 'N quinoline red

Vasser cyanine solution 1: 500 acetic acid solution 1: 500 a 100 cm<sup>3</sup> Dale 1 drop OVEN w 100

cm<sup>3</sup> Ole 1 N O1 cm<sup>3</sup> Å® 100 cm<sup>3</sup> O1 cm<sup>3</sup> 1 R 0: 5 cm<sup>3</sup> d 100 cm<sup>3</sup> Ocean 1 N 1 '00 cm<sup>3</sup> e 100 cm<sup>3</sup>

O1 cm<sup>3</sup> 1 B 2: 0 cm<sup>3</sup>

!) In order to measure these minimal amounts correctly, I prepared a mixture of the normal cyanine solution 1: 500 with alcohol in the ratio 1: 100 and took 1 cm<sup>3</sup> for solution I and 10 for solution II cm<sup>3</sup> after I had convinced myself through multiple tests that an increase in the alcohol content had no noticeable influence.

2) H. W. Vogel: "The Photography of Colored Objects", p. 88.

The various methods of sensitizing gelatin emulsion plates etc. 097

Spectrum recordings using ordinary silver bromide plates, which had been bathed in these solutions, showed that even 1 ° / °, quinoline red (d) caused a maximum in yellow that followed the cyanine maximum and was equivalent to this in intensity with increased addition (c, d, e) extended to E in the yellow-green and then exceeded the cyanine maximum in the orange in intensity. The sensitivity to blue was shown to be increased by quinoline red, so that a plate bathed and exposed in e gave an almost closed band. The least effective was the plate for green between E and F.

I did not get the narrow maximum between A and a with the above azalin bathing plates. The results of my experiments are therefore briefly summarized as follows:

I. Comparison of the methods of Schumann, Weissenberger and Debenham.

1. Schumann's method is uncertain; there are mostly unclean and veiled plates.

2, Weissenberger's method is safe; the plates work very clearly, are quite sensitive, but their sensitivity extends only to blue and a narrow area in the orange between round ones.

3, Debenham's method is safe; the plates are quite pure and very delicate. The color sensitivity extends from red, orange, yellow, yellow-green and blue to dark blue and is only interrupted by minima in red and green between E and F. As a disadvantage of this it should be stated that they must be exposed when wet.

II. Results with variations of Weissenberger's method.

{ When the cyanine content increases, the sensitivity to blue decreases and the sensitivity to orange, yellow, yellow-green and red increases. }

2. The sensitivity for the latter colors, with the exception of the narrow section at A, is weakened in the case of a very high cyanine content due to the shielding effect.

3. Cyanine and quinoline red in acidified solutions sensitize silver bromide gelatin plates in the same way as cyanine alone, using Debenham's method. This method has the advantage over the latter that the prepared plates can be exposed dry. The absence of the minimum at A does not offer any disadvantage worth mentioning.

All experiments were carried out with silver bromide plates from Dr. Schleussner, which are probably best suited for such examinations because of their uniformity and excellent quality. | | In addition to these, I also used emulsions containing chlorine and iodized silver mixed in different proportions, but without getting any more favorable effects. Such records were made for me through the kind mediation of the k. k. Graphic teaching and research institute for these experiments by Dr. Schleussner in Frankfurt a. M. produced and that contained the chlorobromide plates 10, 25 and 50% /, chlorosilver, the iodobromide plates 1% /, iodized silver and the iodobromochloride plates 10, 25 and 50% /, chlorosilver and 1% /, iodized silver.

15th

Explanation of the collotype board (IT board).

No. 5 shows the image of the plate which was sensitized in 0.01% /, dye bath. The dilution

of this mixture is therefore 1: 5000000 (1 g of solid cyanine would be sufficient for 50 hl dye bath of this concentration). In spite of this enormous dilution, there is already an effective strip between C and D, which, however, should no longer be visible in the reproduction. In the negative, the same is still clear in the spectra with 2 and 1 minute exposure, in the one with 1 /

minute weakly, at 1 / minute exposure no longer recognizable. Incidentally, the plate offers almost the same image that a non-sensitized plate would have offered; only the effect in the blue seems somewhat weakened.

No. 4 already shows an intensive effect of the cyanine in the orange and a significant decrease in the sensitivity to blue (cyanine content of the bath 0.1% /).

No. 8 (cyanine content of the bath 1: 0% /,) shows an even greater decrease in the same; on the other hand the occurrence of a maximum between A and a in red and a second in yellow between D and E. The very narrow maximum at A is separated from that at C by a broad minimum in red.

No. 2 (cyanine content of bath 10: 0% /,) shows an intensification of the narrow maximum up to A, while the effect is weakened in all other parts of the spectrum. The maximum in orange and yellow extends further towards Roth to B, in yellow towards E, but is intersected between C and D by a weak minimum; it has the highest intensity between 5 and C in the Roth. In any case,

these phenomena are due to the effect of the screen; the plate also appears heavily colored, which was not noticeable in those discussed earlier. The effect in the blue has decreased very significantly. With the exception of blue, this plate has the sensitivity for a broader range of colors, which is, however, very depressed due to the shielding effect. Attempts to reduce the coloration of the gelatine by adding 2 and 3 drops of acetic acid gave a negative result: the plates worked worse in every respect.

In view of these results, it appears beneficial to use the most favorable cyanine content in the sensitizing bath for any special purpose. In the case of a recording in which the sensitivity of the plate for orange and blue should be the same and as high as possible, a cyanine content of 0-19 will be chosen; = if the color effect should also extend to yellow and red, if sensitivity is secondary, a much higher cyanine content will be chosen (up to 10Å ° /,).

Debenham's method.

In order to extend the effect to a wider range of colors and to obtain very high sensitivity, the use of Debenham's!) Method is recommended. This consists in bathing the plate in an alcoholic cyanine solution! / ,: 480 and, after drying (after a few minutes), bathing it in water for 2-3 minutes and exposing it while it is still wet. A. Under â € œ> the same conditions as No. 2â € "5 spectrum recorded on a plate prepared using this method shows No. 1. All colors, with the exception of a narrow stripe, are red and green to Dark blue and violet Not the last two, which circumstance can be explained on the one hand by the use of the luminous gas flame, which is relatively poor in blue and violet rays, and by the absorption of these rays in the prisms of the Steinheil spectrograph. The sensitivity is very high and that for orange should be the sensitive equal to the ability of un-bathed plates for blue. These plates can therefore be used very well for holding colored objects. The fact that they have to be exposed in a moist state, of course, significantly limits their usability, since on the one hand they may be useless for all those purposes that require great sharpness (for example for microphotography) and on the other hand they are untenable the same prevents their use at work away from home.

!) Photographische Rundschau, 1894, p. 279.

Plate II.

Photographs of the solar spectrum on cyanine-bromide-silver gelatin

plates. Collotype of the k. k. Graphic teaching and research institute in

Vienna.

The effect of color sensitizers on orthochromatic  
plates.Of

J. M. Eder.

(Yearbook for Photography and Reproduction Technology, 1896, p. 166.)

It has been a long time since I completed my comprehensive investigations. He had researched and published color sensitizers on orthochromatic plates. Over the years, I supplemented and expanded my research by occasionally speaking out to ward off erroneous assertions or erroneously carried out experiments and related fallacies.

More recent work, especially by Baron Hübl, confirm my statements and views, insofar as the requirements that I demanded of sensitizers are in accordance with all newer procedures.

A further divergence of my test results with the information provided by Acworth's has recently been clarified by Baron Huebl (*Photographische Correspondenz*, 1895, pag. 550) by proving that Acworth had so-called « Shielding effect of the dye as a secondary influence and that this caused the contradicting results.

I don't need to dwell on this question, all the less since I specified my point of view in Volume II of my "Detailed Handbook of Photography" (2nd edition, p. 39) with the words: "In my opinion, the maximum of the sensitization is always identical to the maximum of the absorption in the colored bromosilver molecule; on the other hand, in comparison to the absorption maximum of the pure dyes, there is a shift in the sensitization maximum according to Roth, because the absorption maximum of the colored bromide silver also shifts in the same sense.

But two other questions are becoming more talked about again, namely:

1. the question of whether the light sensitivity (inappropriateness to light) of the dyes in and of itself has an influence on the strength of the sensitization capacity for silver bromide. I always answered this question in the negative; I could never prove such a regular connection and
2. The question of whether the dye itself is chemically changed (decomposed) during the exposure of colored bromide silver plates and then the reaction product of the decomposed dye photographic image production (reduction) bring about, which view Abney expressed at the time. | | 18 \*

100 J. M. Eder, *The Effect of Color Sensitizers on Orthochromatic Plates*.

These two questions are logically related and several years ago Prof. Vogel had against Capt. Abney polemicizes. My attempts had led me to reject Abney's older hypothesis, and more recently Bothamley took up both questions recently debated in England. | Bothamley first found (*Brit. Journ. Of Phot.*, 1895, pag. 727) that the sensitizing effect of the dyes is not related to the inauthenticity to light. He also found that color sensitization also exerts its influence when the colored plates are immersed in strongly reducing solutions, for example pyrogallol and sodium sulfite. Both cyanin, eosin, rhodamine etc. retain their sensitizing effect. Bothamley concludes from this that it is impossible that Abney's hypothesis "the dye is oxidized by the action of light and the oxidation product reacts secondary to the silver bromide" is true, because this experiment prevents the dye from being oxidized.

Bothamley's arguments are noteworthy. An experiment I did some time ago led me on a very different path. To similar conclusions. A cyanine solution that had been decomposed and browned by the effects of years of light provided me with the experimental basis. This solution obviously contained in abundance the products of the decomposition of cyanine in the light and should therefore give a reduction in contact with silver bromide and subsequent development. With this solution I coated drying plates in the dark and put them in developer without the coated areas having become noticeably blackened. Even adding the exposed cyanine solution to the developer did nothing to change the matter. So I think I can safely assume that the cyanine just as little as the other dyes cause color sensitization through their own chemical

decomposition in the light, but that the theory of the sensitizer effect, which was first established by Vogel and expanded by me, is a consequence of increased Molecular vibration have validity.

About colored light filters for orthochromatic images and three-color printing. Of  
J. M. Eder.

(Photographic correspondence, 1896, p. 483.)

The manufacture of color-sensitive plates has now reached a satisfactory level of perfection; you can purchase dry plates with good sensitivity in green, yellow and orange, or you can make wet or dry plates yourself. Commercially available gelatine plates with yellow-green

Sensitivities that appear analogous to eosin or erythrosin sensitization are Perutz's eosin silver plates, Schleussner's orthochromatic plates, Edward's isochromatic plates, Schattera's eosin plates, Smith's orthochromatic plates, the latter being yellow. Contain dye over the sensitized plate, which mutes the blue and washes off as it develops. Perutz azaline plates (colored with cyanine-quinoline red) and Lumiere's panchromatic plates, which behave quite analogously, would be mentioned as commercially available orange-sensitive plates, which are also sensitive to yellow-green. Pure cyanine plates are most sensitive to orange-red; But they are not commercial products, although it is likely that they can be fabricated to be sufficiently durable if the cyanine is decolorized with acids (using Weissenberger's method); when using volatile acetic acid, the plate automatically becomes sensitive to orange when it dries out; if non-volatile acids were used, the plate would not be sensitive to orange until the plate was bathed in an alkaline bath. A fluorescein plate (bathing plate or similar to Debenham's cyanine process) or an acridine yellow plate could be used as the green-sensitive gelatin dry plate.

In addition, there are the very powerful orthochromatic Collodion emulsion processes. Albert's emulsion, sensitized with dye P, works in the same way as an eosin silver collodion emulsion (sensitivity to yellow-green); more recently Albert has brought a dye for his emulsion into the market, which further sensitizes against orange. Fluorescein-bromide-silver-Collodion bathing plates work well for green; for orange-yellow: rose bengal; for orange red: cyanine. Wet iodized silver collodion plates only show the effect of the blue-violet rays.

If necessary, special colored light filters are to be added to all of these color-sensitive plates if one or the other color is to be suppressed. If you want to achieve a harmonious effect in a single picture (for a monochrome print or an ordinary photographic copy), no color must be completely removed by the light filter.

deleted, but at most dampened; this can be achieved with light yellow filters, for example<sup>102</sup> J. M. Eder.

Picric acid or Martius yellow, or in special cases with dark yellow (red-yellow) layers, for example aurantiacollodion, solutions of potassium dichromate etc.

More information about these colored layers will follow later.

Only a few peculiarities of the two main types of light filters used in practice should be pointed out here.

They are first produced by pouring colored collodion or colored gelatine over plane-parallel glass plates. The former is suitable for alcohol-soluble dyes and is generally known, the latter for water-soluble and has been described several times. In the latter case, I pour clear, well-filtered gelatin solution over the horizontally leveled glass plates, which incidentally contains the concave which. in. the gelatine dry plate manufacture: - is; . It is advisable to add a few drops of acetic acid to the gelatine, as this makes the gelatine more fluid and more homogeneous. As soon as the gelatin layer has dried, it is bathed in aqueous dye solutions, rinsed off and dried.

For light yellow you bathe in picric acid solution, for golden yellow in Martius yellow (absorbs more strongly against blue-green than the previous ones); for orange-yellow in  $\beta$ -naphthol orange, for red orange in erythrosine. I do not want to call these dyes finally chosen; after all, they are easy to use. For light yellow filters, I use picric acid alone and have two such plates cemented. For: golden yellow, a Pikringelb and Martiusgelb plate each is cemented or a gelatinized plate is first colored yellow in picric acid, dried and then bathed in Martius yellow. Both types of plates attenuate the blue-violet well, but to different degrees. If the blue-violet and light blue are to be cut off completely, then a gelatinized plate colored by bathing in  $\beta$ - naphthol orange can be used, but it must be combined with a picrin + Martius yellow disc, because the spectrum analysis shows that naphthol orange is blue-violet which has to be absorbed by the yellow colors mentioned. A single plate can also be used by first coloring a gelatinized plate in Martius yellow (or better picric acid, then Martius yellow), rinsing it, drying it and then bathing it in B-naphthol orange, rinsing it again and drying it. These orange-yellow plates cut away the blue-violet sharply and with eosin or erythrosine plates only leave the yellow-green, with fluorescein or acridine yellow plates, only the green comes into its own.

If you combine the aforementioned, multi-colored orange plate with a layer colored in erythrosine, only the red and orange come into their own (with cyanine plate).

When using such colored and cemented colored glasses, errors can occur which are noticeable badly with three-color printing. If the plane-parallel glasses are too thin, they bend. when cementing, damage the sharpness of the image and change the focal distance; the same can happen if the gelatine is poured in different ways. This phenomenon occurs with different glasses in different thicknesses and causes the creation of different image sizes with the setting remaining constant, an error which the matching of the color components

prevents polychrome prints. I observed the occurrence of a fluctuation in the image distance (setting "in the same size, with a focal length of the objective = 60 cm) by 1" cm in a special case. One must beware of such errors to guard.

Secondly, plane-parallel tubs are used (we work with an excellent one of this kind of 1 cm Blüssiskeitsdickers from Br. Steinheil in Munich> also ZeissÄ ± in Jena and Re Britsche in Vienna. can be easily eliminated, even if the vanne were inadequate (that is, the focal distance would change due to the curvature of a poorly leveled surface), if one takes all exposures through the same vat blue-violet ray component serves best common iodine collodion in the wet process without the application of any colored screen. If you want the mistake of an imprecise Eliminate glass wall, take the setting with the upstream tub, which is with pure

About colored light filters for orthochromatic images and three-color printing. 103



Water is filled before; Likewise, the image is made with iodine collodion and then the other images are made on appropriately sensitized, color-sensitive plates using colored aqueous fluids; the application to liquids other than water is self-evident. A Using this working method, at the k. k. Graphic teaching and research institute in Vienna made several reproductions of very difficult to pick up colored objects (oil paintings, miniatures on ivory and porcelain, polychrome fabric) with very good results. Thirdly, colored light filters (cemented glass plates) should be mentioned, which are produced in America by John Carbutt and by the Hemsath company in Frankfurt a. M. come on the market in Europe. The to the k. k. The light filter collection received by the Graphic Education and Research Institute in Vienna consists of a dark blue, a green and a deep red square pane of glass with a side length of 10 1/2 cm. The color is correspondingly pure and the brightness of the glass panes moderate, which can be explained by the fact that actually narrowly delimited spectral regions come into their own. Green light filters are not required to photograph the green light component of a colored object if green-sensitive plates (which lack red sensitivity) are used in combination with yellow plates; in a similar way, blue light filters are unnecessary as soon as plates are used which are only sensitive to blue-violet. The Carbutt's colored light filters are obviously intended for panchromatic plates or those which are sensitive to orange-red, green and blue-violet at the same time, but they can also be used in combination with partially color- sensitive plates. However, all of this work can only be carried out efficiently using the spectroscope.

Plates sensitive to red by means of cyanine, cerulein and nigrosine. Of Wilhelm Eckhardt.

(Photographic correspondence, 1897, p. 124.)

The production of red-sensitive plates presents greater difficulties than the sensitization for green, yellow and orange, for which the latter in the eosins, acridine dyes etc., good sensitizers have been known for a long time. To increase the color sensitivity for yellow and orange, mostly cyanine is used, for which dye H. Hinterberger has determined the most favorable working conditions!) And about which Baron Huebl also made very interesting observations. Sensitizers that can be used in practice, which make silver-bromide plates sensitive from orange to extreme red, have not yet been investigated with the same degree of accuracy, although several works of great value have been published in this regard; therefore, at the suggestion of the government councilor Prof. Dr. J. M. Eder at the k. k. Graphic teaching and Versuchsanstalt in Vienna carried out a series of spectrographic and photochemical experiments, which included some of the best known sensitizers for the less frangible spectral regions. It is known of Coerulein that it can sensitize bromosilver gelatine down to dark red to Fraunhofer line A, while Nigrosin D has been shown to sensitize from orange to red in three maxima °). I did not immediately get the expected results with either dye; nigrosin B did not provide enough pure plates, while cerulein is very unstable and decomposes if the plates sensitized with it do not dry quickly enough. This latter circumstance led me to a new kind of sensitization to my

knowledge, namely to dye the plates in aqueous dye solutions and then to bathe them in alcohol. I get dry records quickly, free from excessive shot dye. The alcohol no longer dissolves the dye bound by the bromide silver. Cerulein plates.

The Cerulein S (obtained from Dr. Schuchardt in Görlitz) sensitizes bromosilver gelatine dry plates in such a way that they have two clear sensitization bands; one in the Roth

1) Cf. p. 95 of these treatises. 2) cf. p. 60 of these treatises. ⑧ Photographic Correspondenz, 1896, p. 116.

Plates sensitive to red by means of cyanine, cerulein and nigrosine. 105

from the Fraunhofer line A to C (maximum between a and B), the second from C  $\frac{1}{2}$ , D to a little yellow-green with a maximum in C  $^{\circ}$   $\frac{1}{2}$ , D.

The following recipe gave me the best result:

Coerulein 2 parts \ Nassepset se. 2 77 rel)  $\hat{A} \in \sim R AO$

TAKE ee 2 |  $\hat{A} \in \infty$

The aqueous dye solution lasts for a few days, the diluted solution with ammonia must be used immediately. |

The silver-bromide gelatine plates are bathed in this for 3–4 minutes, drained after removal and then placed in alcohol for 3–4 minutes. Move the cup a little before removing it from the alcohol. When the plate has drained well, place it on blotting paper to dry. Finger grips inevitably stain. Development takes place as usual; a little

Adding bromine to the developer works

favorably. Nigrosine plates.

Nigrosin B from the Elberfeld paint factory, formerly Bayer & Co., exceeds that. Coerulein has three times the sensitizing effect for Roth. But nigrosine plates require much more careful handling than cerulein plates. The spectrographic examination of the nigrosine plates showed three sensitization maxima. The first, very strong, awareness tape begins before the Fraunhofer line A, rises steeply and falls steeply at B; the second, weak band is in C and the third ranges from C  $\frac{1}{2}$ , D to a little above D with a maximum at C  $\hat{A}^{\circ}$   $\frac{1}{2}$ , D.

The aqueous storage solution 1: 500 lasts about 2 weeks. For use I

take: Nist 1a 9 12500 7 22 2er neile Sasse ee errli y x

Anmoma kerton web 1 z

A lower amount of dye decreased the sensitivity to Roth, while a larger amount of dye did not increase it any further. More ammonia made the sensitivity marginal, but it did lead to haze. The above nigrosine solution must be filtered before use and used immediately. Bathing the silver bromide plates in the dye solution and treating them with alcohol is the same as with the cerulein plate, only the movement of the cup when bathing in alcohol has to be much more abundant. If you want to keep the alcohol for later use, you can rinse the plates after the dye bath. The alcohol can now be stored for further use, but must then be filtered each time. The panels can still be exposed when damp

become; the dry plates can be kept for 8 days.

Sensitometric tests with different red sensitive plates.

To determine the influence of the dyes on the overall sensitivity of the silver bromide plates, experiments were carried out using Scheiner's universal sensitometer!).

1) Eder: "Detailed handbook of photography", 2nd ed., Volume II, pag. 20. Scheiner's universal sensitometer is particularly suitable for such experiments because the light rays from the normal light source fall completely freely on the sensitized layer, without any absorbent layers in between. Photographic correspondence, 1894, p. 4833, 14th

106 Wilhelm Eckhardt.

This should make it clear whether the dyes, as is the case with cyanine plates, for example, increase the relative sensitivity to red, but reduce the overall sensitivity to a greater or lesser extent. The uncolored silver bromide emulsion and an eosin bathing plate were used as comparison objects. This eosin bathing plate was made in such a way that 3 parts of an eosin solution (1: 500

) were used as a sensitizing bath with 100 parts of water and 1 part of ammonia; in this the plates were bathed for 3-4 minutes and then placed in alcohol in the manner described above and dried.

I also included cyanine plates in the group of experiments using the Weissenberger method!) And plates bathed in cyanine-borax solution?).

The table below shows the relative sensitivity to candlelight (petrol candle). Table.

Relative sensitivity of the silver bromide gelatine plates bathed in the following dye solutions, based on an uncolored bromide silver plate.

a TE

Ordinary bromide silver plate ... 1 OS N EN ee Cyani  $\pm$  mniakssivsaren 2, 0 0 ie Gyanmnema Borse name Im: Soctul a ne a ee er Niakos ne ee ee. ee

It follows that eosin increased the overall sensitivity of the plates, while cerulein and nigrosin depressed the same, if only slightly; very significant is the loss of total sensitivity when using cyanine.

Sensitometric experiments on the sensitivity of different plates behind red, blue and green light filters.

Since it is important for three-color printing to get to know the relative sensitivity of different types of plates behind different colored light filters, I made a series of sensitometer samples in such a way that I placed blue, red and green panes of glass between the light source and the plate. The American "Carbutt three-color screens" were used for this purpose because they have a deep red, free of yellow (from A to C1 /, D), a fairly pure green (from D to ER) and a blue-violet (from F to H). I mention the type of color filter in more detail because the relative sensitivity of different types of plates is subject to strong fluctuations, depending on the nature of the light filters, which, as is well known, opinions differ widely about the best properties. The following table shows the relative sensitivity of bathed silver bromide plates behind the light filters described above.

DECYani  $\pm$  e2D0 0m ee a part of the mass esse. 500 = Be siosaume ae rn a drop:

⑧) Cold saturated borax solution. 100 parts Cyanine ± m SU 0  
 a er ale Bath for 5 minutes, rinse and dry.  
 Plates sensitive to red by means of cyanine, cerulein and nigrosine. 107

Table II. | Relative sensitivity of the different types of plates behind blue, green or red  
 panes, based on an ordinary silver bromide plate without a filter - 1. Light source: petrol  
 candle. TTS SG â € "â €" eb always sell Balareeso ne blue green | Roth Ordinary  
 bromide silver plate. . he Be â  
 € "Kos ee ee le â €" @ yanÄ ± n with acidic acid a. 0 ... De an a Sole Can mieBore  
 ae ale | â € "Spur Coerulena Sasse Le ea at: en alae Nierosime Besen ro Peer In Er  
 ER

This table shows that placing the blue glass in front of it reduces the light effect to one  
 eighth, that the eosin plate has the same sensitivity to blue light as the uncolored plate  
 and that the nigrosin and cerulein plates are noticeably more sensitive to the blue  
 radiation areas, if not significantly, have suffered. In contrast, the cyanine plates had  
 become significantly less sensitive.

As was to be expected, the eosin plate showed the greatest sensitivity to green of the  
 types of plate tested; However, the exposure time was at least 11 times longer than with  
 the usual plate behind the blue pane.

In terms of Roth sensitivity, the nigrosine plate is superior to all other plates, in that  
 when gasoline light is used, the exposure time behind the Roth filter only had to be  
 about 13 times longer than for the blue plate. | |

The cyanine plate gave the worst results in these experiments, namely hardly a trace  
 of the image, which can be explained by the fact that the Carbutt red disk I used cuts  
 off yellow and orange strongly, so that the orange sensitivity of the cyanine plate is not  
 at all could come into its own.

The cyanine plate is therefore unusable for such color filters; only if one conducts the  
 cyanine preparation in such a way (see Hinterberger, p. 95 of these papers) that the  
 second maximum of the sensitization, next A, emerges, one obtains a photographic  
 effect behind dark red-  
 discs, but such negatives are usually powerless.

Changed behavior of sensitized plates to electric light.

When I wanted to use the relative exposure times of the types of plates described behind the various filters, obtained in this way with Scheiner's sensitometer using the petrol candle as a light source, to take pictures of paintings under electric light, the calculated exposure times did not at all agree with that. Coincidence. The reason is that the brightness distribution of the colors in candlelight and

and electric light is significantly different, namely the exposure behind the Roth disk must be taken 4 times longer when using electric light than calculated after the experiments with the petrol candle; the electric. After all, light is relatively poorer in red rays and richer in blue rays than petrol candlelight. The following table gives the relative exposure times for electrical equipment Ziemer's, which can be used in practice. 147

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108 Wilhelm Eckhardt, Roth-sensitive plates using cyanine, cerulein and nigrosine.

| Table IM: Relative exposure times of the various types of panels to electric light and use of the American "carbott three-color screens", based on an ordinary silver bromide plate without

Table 4: Relative exposure times for various filters in a filter plate type Bee RE BE er ern, Blue Green Red Ordinary bromide silver plate. . ER \_  $\hat{=}$  "osin Er N neen = Be Eoerulenesy eenee  $\hat{=}$   $\hat{=}$  "1300 NienosinaDr a een nen \_  $\hat{=}$  "400

From these experiments it emerges that for an accurate assessment of the capacity of a dye for practical photographic recordings, not only the sensitization curve has to be taken into account, but also the influence on the absolute sensitivity, the light permeability of the color filter for rays of certain Wavelength and the quality of the light source. These factors are now sufficiently precise for the dyes mentioned above due to the experiments described

ensured and therefore usable in practice.

Investigations into the sensitization ability of various tar dyes for silver bromide gelatine drying plates.

Of

E. Valenta.

(Photographic correspondence, 1897, p. 129 and 185.)

In the photochemical laboratory of the k. k. At the graphic teaching and research institute in Vienna, I developed a number of newer tar dyes, mostly blue, green and violet dyes, which the companies: Actiengesellschaft für Anilinfabrication in Berlin, C. Bayer in Elberfeld, Meister,

Fokus and a € šBrÄ¼nnens Ins rRlochseva = N . 7 Cassella in Sick Turtle, Durand Huguenin ' & Co.,]. Geiey in Basel, Society for Chemical Industry in Basel'u, A. of the Directorate of the k. k. Graphic teaching and research institute made available in a lovable way, examined for their usability as optical sensitizers. These examinations are usually carried out with the help of the spectrograph using sunlight, because as daylight this represents the main type of lighting in photographic recordings and because, on the other hand, the Fraunhofer lines are a good means of orientation for the spectrum.

Since I couldn't count on having sunlight available in case of need, because of the bad weather and the unfavorable light conditions in winter, I conducted the described sensitiser tests in the light of a 30 candle Siemens gas burner and a sodium flame with the little Steinheil's spectrograph. The purpose of switching the sodium flame into the beam path was to introduce the sodium line into the continuous spectrum of the Siemens burner flame for the purpose of orienting the negatives.

The tests were carried out in such a way that with the same distance between the burner and the slit of the spectrograph and the same slit width, the plates to be examined were sensitized by bathing for 3 minutes in the dye solutions in question and then dried for 5, 10 , 30, 60 and 300 seconds exposed and, in order to establish the sensitivity ratios in the blue-green part of the spectrum, were compared with a silver-bromide gelatine plate of the same provenance that had been exposed for the same length of time. The results obtained are therefore completely comparable and I intend to use this mode of observation, even though the light from the Siemens burner does not match the light of the sun in terms of its composition, for the sake of comparability in the further series of tests that I intend to keep.

Leopold Cassella's in Frankfurt a. M. produced diamine dyes: diamine blue, diamine green, diamine steel blue, diaminogen blue, diamino blue were found to be used for the purpose of sensitization

110 Eevakenta.

Enlargement of bromosilver gelatine plates was unusable because they showed only a weak continuous sensitization without showing a maximum of the effect or a strong band in the yellow, green or red parts of the spectrum.

The blue dye naphtindone 2B produced by the above company already causes strong fogging in concentrations of 1: 20000, but a band from C to C3 /, D is clearly recognizable with prolonged exposure. With very strong dilution (1: 200000) it works better, but is not usable in practice because of the general sensitivity is pressed hard and the tape does not protrude sharply. Likewise, another dye, the M ethylindone DB from the same company, causes a band between a and B to appear when strongly diluted (1: 200,000 to 1: 500,000), but the sensitivity is also greatly reduced.

Rosindulin, which in its simplest form has the formula:

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ee, 6

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at the time?), was brought onto the market on a trial basis by Kalle & Co. at the time; the same, or its sulphonic acid, has the property of coloring bromide silver only to a very slight degree; nevertheless, like some of its derivatives, which have this property to a large extent, it is a

sensitizer, which the bromide silver of gelatin dry plates for Sensitizes the yellow and yellow- green rays from D to D', E (maximum DJ, E). The disulfonic acid of phenylrosindulin, which is marketed under the name of Azocarmine?), Dissolves in water or alcohol (spirit-soluble preparation) with a blue-red color and this solution works very strongly (1 : 200000) sensitizing without the addition of ammonia in such a way that a weak band appears in the red from A to a and also becomes visible in DJ, C.

It should be noted that azocarmine tolerates a combination with eosin and, with the use of very small amounts of eosin and sufficient exposure, produces almost closed spectra at D with the second maximum from A to a. In a higher concentration, the azo carmine has a worse effect in the ratio 1: 10000 there is no longer a maximum, but only continuous, faded spectra even with long exposure. |

Naphtyl blue and naphtyl violet work better than rosindulin and azo carmine. These dyes, which are available in the form of dark brown powder from J. Kalle & Co., Biberich a. Rh., Are marketed, are rosindulin dyes, which are derived from Naphtylroth and can be regarded as phenylated derivatives of this body?  $\hat{\Delta}^{\circ}$ ). The formula belongs to the naphthyl blue

at  
nn  
(a 6 5  
An  
s  
6th

) Giorgiewics: "Textbook of Color Chemistry", 1895, pag. 209. 2), Same, pag. -216. 2) The same, par. 217.

Investigations into the sensitization ability of various tar dyes etc. all while with naphthyl violet in the group he anostellerdes  $\hat{\Delta}, \neg$ , Hl, a hydrogen init,

The effect of the two dyes on silver bromide gelatin plates is almost the same. In the former, at dilutions of 1: 200,000 to 1: 400,000, a band appears, extending from D to above C, which runs very weakly towards the more frangible part; the maximum lies between C and D.

In the case of naphthyl violet, under the same conditions, the sensitization band starts at C1 /, Band is sufficient. Over 2 hmaus,

The Magdalaroth, which is related to the named dyes and its composition through. the formula The EN S> 2 a e

on  
VE INE  $\hat{\Delta} \in "$  |  
| - N - |  $\hat{\Delta} \in "$  NH, SS | 4th  
of:

illustrated, was examined by Eder at the time  $\hat{\Delta} \in$ ); there is a strong maximum of the yellow effect at D, which runs towards the breakable end of the spectrum with long exposure with a weak green effect (E den).

The azindone blue G, which is close to these dyes, depresses the sensitivity of the plates very strongly and has a fogging effect, even when very diluted; reaching above D, while in higher concentrations it produced no sensitizing effect.

This way. Benz d miarb or ee 0020 Benzopurpurin, Bordeaux extra and Naphthol- red were investigated by J. M. Eder at the time: and did he get very good results when using ammoniacal sensitization baths?). Eder found that these dyes only increase the light sensitivity of the bromide silver in green to yellow or orange (E to over D).

The congorubine that I examined, which the Berliner Actiengesellschaft für Anilinfabrication made available to us, shows a broad band of sensitization when exposed for a long period of time, which is very strong and has its maximum at D; it ranges from C to m. "and thicker, this tarbsÄ ± om which goes further into the red than the above dyes and whose use does not reduce the overall sensitivity very much, be of value for practical purposes.

The following rule turned out to be best: 10 cm? Dye solution 1: 500, 2cmÂ® ammonia and 200 cm? Water. With longer exposure, a band is obtained which, apart from a weak minimum in front of E, extends from violet to red (above C) and has a strong effect.

Of other dyes in the Congo series, we mention Zambesi blue B and Chicago blue B, both azo dyes of the Congo series, produced by the Berliner Actiengesellschaft für Anilinfabrication. The Zambesi blue B gives in concentrations of 10 cm? the solution 1: 5 00 to 100 cm? Water and 2cm? Ammonia is a weak band which cuts off and cuts off in theinfrared outside A

Stronger broad band from a to DY, E, which bands, however, only become apparent with longerexposure.

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1) Eder's "Detailed Handbook of Photography", IH. Theil, 1890, p. 131, 2) Eder's "DetailedHandbook of Photography", III. Theil, 1890, p. 168, 12 E. Valenta.

step and are blurry. Chicago blue shows a similar behavior, only the first weak band is missingand the band from A to D is much weaker.

Several dyes, which were made available to us at the time by the Basel Society for Chemical Industry, turned out to be sensitizers; According to the manufacturer, the dye violet P is the HC / salt of tetramethyldiamidotrioxetriphenylcarbinol and a derivative of pyrogallol. It works in concentrations of 0 ': 5 cm? the solution 1: 500 with 200 cm? Almost no water, on the other hand with a higher concentration (20 cm? Solution 1: 500 with 200 cm? Water) a band occurs which extends from C to CY /, D with longer exposure. However, at this concentration of the sensitizing bath, the plates already show a tendency to form a haze.

Violet DP is already effective in dilutions of 10 cm? the solution 1: 500 with 200 cm? Water strongly pressing on the general sensitivity of the plates, on the other hand in dilutions (0: 5 cm? The solution 1: 500 with 200 cm? Water) much cheaper; there is a strong band from B to D and a weaker band, reaching up to D1 /, E, with longer exposure, while the overall sensitivity is only slightly depressed.

Violet R is the H Cl salt of tetramethyldiamidooxytriphenylcarbinol. Stronger concentrations have an unfavorable effect on these dyes too and a strong band from B to D! /, E only appears when the dye is highly diluted, with two maxima, a strong one slightly above C and a weak one, with shorter exposure D, reveals.

A very good effect was achieved with the use of tetraethyldiamidooxytriphenylcarbinol (HZ Cl salt) and strong dilution (0Â ° 5 cm? Of the solution 1: 500 to 200 cm? Water). You get a strong band that starts at B and extends from C to C? /, D; with shorter exposure only the maximum at



C! /, D. emerges. In the case of very long exposures in sunlight, the effect appears to run into the infrared and a weak band outside A can be seen.

In combinations with extremely small amounts of eosin (0.201 of the solution 500 BosÄ ± n and 0.5 of the solution 1: 500 of the dye with 200 cm<sup>3</sup> Water), plates can be obtained which work well in orange-red as well as green-yellow and blue.

Dimethylmonoamidodioxytriphenylcarbinol (soluble in water) is a derivative of resorcinol and has a far less favorable effect; it occurs at a dilution of 0.5 cm<sup>3</sup> the solution 1: 500 with 200 cm<sup>3</sup> Water out a blurry band at DY, E, while hints of a second band between C and D can be seen.

The dimethylmonoamidotrioxotriphenylcarbinol (HCl salt) gave no result at all, but rather a gradual sensitization without a maximum can only be detected with longer exposure.

In addition to these dyes, a dye of unknown constitution, which was obtained from pyrogallol disulfonic acid in a sodium-alkaline solution (blue body soluble in water with a yellow-green color), was investigated, which at a dilution of 10-20 cm<sup>3</sup> the solution 1: 500 with 200 cm<sup>3</sup>

Water only gave a very blurred band at D1 /, E, furthermore the chlorozinc double salt of dimethyldiamido-orthoditolylidichlorodiphenylmethane (symmetrical), called firm salt, and that of tetramethyldiamidobenzhydrol, which is called hydrolein.

The firm blue had no effect, while hydrolein at a dilution of 20 cm<sup>3</sup> the solution 1: 500 with 200 cm<sup>3</sup> Water produced a rather strong but narrow band from C to CÄ °? /, D (maximum C! /, D). Incidentally, the dye is of no practical importance because it greatly reduces the sensitivity of the plates and the solution decomposes within 24 hours.

A rather powerful effect was achieved with Acid Violet 5B from F. Bayer in Elberfeld.

When using this dye, the concentration has little influence, the addition of ammonia (2 cm<sup>3</sup>

Investigations into the sensitization ability of various tar dyes etc. 113

on 100 cm<sup>3</sup> the dye solution) works favorably. If there is sufficient exposure, the sensitization band extends from C to almost D.

The Farbwerke Meister, Lucius and BrÄ¼nning in HÄ¼chst a.M. bring a disazo dye made from diamidophenylazindobenzene on the market (D. R. P. No. 86225 ex 1896). It is a dark, dough-like mass, which is soluble in water with the addition of ammonia with a green color. The solution of the dye sensitizes

the plates for Roth; the best effect was with a solution of 15 cm<sup>3</sup> (1: 200) and 200 cm<sup>3</sup> Water achieved. With sufficient exposure, a strong band from a to CÄ® /, D is obtained, while very dilute solutions do not produce any sensitization.

Less favorable results were obtained with the dyes belonging to the patent blue group. Patent blue does not work in strong dilution, in concentrations of 10-20 cm<sup>3</sup> the solution 1: 500 by 200 cm<sup>3</sup> Water there is a narrow band between B and C. Wool green shows the same behavior and has an even less favorable effect on reducing sensitivity. Cyanol (Cassella) only resulted in continuous sensitization, as did azo green from the Badische Anilin- und Sodafabriken.

The group of alizarin dyes is from Dr. Eberhard (Photographische Correspondenz, 1896) has been examined in great detail; I just want to add my observations on the alizarin green S to these investigations. This doughy dye dissolves in water with the addition of ammonia with a green color. The solution (4g in 500 cm<sup>3</sup> Water mixed with the necessary amount of ammonia), diluted with water in a ratio of 1:50 to 1: 100, gives a sensitizing bath which makes the plates treated with it sensitive to Roth makes. Very good results are achieved with the fresh dye

solution. The awareness band goes from A to C  $\frac{1}{2}$ , D and is very strong; unfortunately the ammoniacal dye solution doesn't last long.

Another useful sensitizer would be the blue dye sold by Kalle under the name "Biebericher Indigo 5", which has a strong band from C to C  $\frac{1}{2}$ , D and a weaker band to D  $\frac{1}{2}$ , E there. The presence of small amounts of silver nitrate in the bath is beneficial. The dye works very well in a strong dilution (0.5 cm<sup>3</sup> Dye solution 1: 500, 2 cm<sup>3</sup> Ammonia and 2 drops of 10% silver nitrate solution); Without ammonia and silver nitrate, long exposure results in a band at B in addition to the above, which, running to both sides, is faintly contrasted.

The cressyl violet produced by the Mählheimer Farbwerke; BBA gives in a concentration of 0.5 cm<sup>3</sup> (1: 500) on 200 cm<sup>2</sup> Water a band from C to C  $\frac{1}{2}$ , D, but the general sensitivity is strongly reduced. The sensitivity of the plates is depressed to a greater degree by the blue dye Capri blue, which belongs to the same group and which only produces a narrow band at B when extremely diluted, while greater concentrations produce a strong haze as a consequence. A green dye sold by the Badische Anilin- und Sodafabriken under the name "Neptungrün S" is only effective when the concentration of the sensitizing bath is higher (20 cm<sup>3</sup> Of the solution 1: 500 by 200 cm<sup>2</sup> Water). You get a strong maximum of sensitization at A  $\frac{1}{2}$  and the general sensitivity is little depressed.

The dyes Eriocyanine and Erioglaurine, brought on the market by J. Geigy in Basel, have a sensitizing effect on the red part of the spectrum. Both require, if they are to be useful, concentrations of 20 cm<sup>3</sup> (1: 500) on 200 cm<sup>2</sup> Water.

Eriocyanine enters

fairly strong band from B  $\frac{1}{2}$ , C to C  $\frac{1}{2}$ , D, while the erioglaurin sensitizes from A to B  $\frac{1}{2}$ , C.

About the sensitizing effect of some tar dyes on bromide silver collodion plates. Of

E. Valenta.

(Photographic Correspondenz, 1897, p. 436; "Atelier des Photographes", 1897, p. 91.)

As you can easily convince yourself through experiments, the effect of different optical sensitizers is often different, depending on whether you use silver bromide gelatine or collodion emulsions. This is probably due to the fact that the coloring properties of the different coloring agents for gelatine and collodion are very different; In addition, the thickness of the emulsion layer in gelatine plates is much greater than in collodion emulsion plates, which means that, provided that the coloring properties of one dye are the same for both substances, a certain area of the gelatine plate with the same concentration is far more dye can absorb than the same large area of the bromide silver collodion plate.

For the experiments described below, a silver oxide ammonia bromosilver collodion emulsion was used, which was prepared according to the method described by Dr. Jonas!), But using equivalent amounts of bromine zinc instead of bromine ammonium and after washing and re- dissolving in alcohol ether with added narcotine (0.5 g per liter emulsion) was allowed to ripen. The emulsion, sensitized with eosin silver, gave strong, clear negatives and was relatively sensitive. |

For the tests, the panels were placed in the solution of the dye in question for 2 minutes after they had been poured They were bathed, then rinsed and placed in a silver nitrate solution 1:

4000, in which they remained for 12 minutes, after which they were exposed when wet. The Hübl'sche 'glycine developer served as the developer. |

The following had a powerful effect: tetramethyldiamidooxytriphenylcarbinol, which is marketed as violet R by the "Society for Chemical Industry in Basel", and the ethyl compound (ACI salt) corresponding to this dye.

With the former dye, the best results were obtained at dilutions of 1: 100,000. The red and orange-yellow effect is greater in the same than the effect in the blue-green and blue. You get two maxima, one of which lies at C and the other between D and E. A longer exposure results in an almost continuous band, reaching from A to F, whereupon a minimum can be seen

is followed by the weaker bromide silver maximum. The analog behavior shows that

!) Eder: "Yearbook for Photography and Reproduction Technology", 1892, p. 35. About the sensitizing effect of some tar dyes etc. 115

Tetraethyldiamidooxytriphenylcarbinol, while when using dimethylmonamidodioxxytriphenylcarbinol two maxima occur, but are almost impossible to determine, although the effect in orange-red and yellow is almost the same as that in blue-green when using this dye. The most effective. The dilution here would be 1: 200,000.

The symmetrical dimethyldiamidoorthoditolylidichlorodiphenylmethane, which is marketed as firm blue by the factory mentioned, shows only very weak sensitizing effects and is very strong in the sensitivity, so that this dye cannot be used. |

The behavior of the blue and green diamine dyes is interesting, like the one from the colorworks Leopold Cassella & Comp. be put on the market.

These dyes are polyazo dyes and give almost all of them useless results with drying plates, while they, when used in the manner described for bathing collodion emulsion plates, mostly produce powerful effects in orange-yellow and red. Do these dyes require concentrations in which their application on gelatin dry plates is not possible, namely 40-50 cm? the solution 1: 500 by 200 cm? Water.

At this concentration, diamine blue gives a broad band in bromosilver collodion plates, which extends from a to E with longer exposure and in which two maxima (one at C and another between D and E) stand out faintly. Diaminazo blue behaves analogously; the strongest effect was achieved by diamine steel blue, in which the red effect exceeds the bromide silver maximum; you get a longer "Beltchtuns za broad sensitization band, which extends from A to F, but only reveals a maximum at B to C. |

Diaminogen blue was also found to be a sensitizer for silver bromide collodion emulsions. There were baths of 1, 10, 20, 40 and 80 cm? the dye solution 1: 500 with 200 cm? Diluted water used. It was found that with greater dilution, analogous to the bromosilver gelatin dry plates, only a weak continuous sensitization to the infrared is achieved; as the concentration of the dye bath increases, the blue effect of the bromide silver fades into the background and a strong maximum comes to the fore at 5.

At a dilution of 40: 200, if the exposure is long enough, a broad band from A to DY, E is obtained, from there on to the maximum of the bromide the same runs and still has an effect, albeit weaker; at 80: 200 only this band remains and the general sensitivity of the plate is so much reduced that the bromide-silver maximum only comes into play after long exposure, while the sensitization band is quickly and strongly noticeable.

Other polyazo dyes were investigated: Chicagoblau (Berliner Actiengesellschaft für Anilinfabrication) requires a concentration of 40 cm<sup>3</sup>. Dye solution (1: 500) on 200 cm<sup>2</sup> Water; a wide band occurs, from a to D! /, E (with longer exposure), with a maximum between C and D. The general sensitivity is strongly depressed.

Zambesi Blue (from the same company) behaves similarly, but reveals two blurry and indistinct maxima.

Tabora black sensitized in dilutions of 10 cm<sup>3</sup> the solution 1: 500 to 100 cm<sup>3</sup> from B to E /, F, the effect is weak with a dilution of 20: 200, with a greater concentration an indistinct maximum emerges. Like the Nianza black, this dye has little effect and has a very strong negative effect on the sensitivity of the plates.

The dyes of the congo group have also proven to be useful sensitizers. Congorubin from the "Berliner Actiengesellschaft für Anilinfabrication" works in dilutions of 20 cm<sup>3</sup> the solution 1: 500 by 200 cm<sup>3</sup> Water strengthens ig. You get a band from B! /, C to D,

with a maximum at C1J /, D. 10%

116 E. Valenta, on the sensitizing effects of some tar dyes etc.

The blue effect is very strongly depressed and only comes into its own with longer exposure. |The best recipe for making a sensitizing fluid with this dye is as follows:

20 cm<sup>3</sup> Solution of congo rubin (1: 500) 200 cm<sup>3</sup> Silver nitrate solution (1: 2000).

Finally, cressyl violet and a new disazo dye made from diamidophenyl azo ± midobenzene were investigated.

Cressyl violet has a sensitizing effect on collodion emulsion plates in concentrations of 1: 200 as well as in stronger solutions. With longer exposure an almost continuous band appears, extending from 5 to violet, in which a maximum at C1 /, D and a maximum between D and E can hardly be established.

The one from Meister, Lucius and Brünning in Höchst a. M. Disazo dye, D.R.P. No. 86225, has a similar effect to that of silver-bromide gelatine plates, only the effect is much weaker. You get a band, from a to C? /, D, with you even at Concentra-

tions of 40 cm<sup>3</sup>: 200 rather indistinct maximum for

CD. The oxamine dyes as optical sensitizers.

Of

E. Valenta.

(Photographic correspondence, 1898, p. 198.)

Almost all of the oxamine dyes brought onto the market by the "Farbwerke Friedrichsfeld" company (Dr. Paul Remy in Mannheim) turned out to be optical sensitizers for bromine. silvergelatin dry plates.

Some of them gave very good results and should surpass the red sensitizers in use today in terms of purity and sensitivity of the plates.

These dyes tolerate the addition of ammonia without being decomposed.

Experiments were made with the following oxamine dyes: Oxamin red MF gave two bands, one at C9 /, D, the other from Dbis / via PD, #. Oxaminreth>, broad band from C to over D, with a strong maximum at D. Oxamine scarlet B, very strong band from 0 ,, D to Â ° C, maximum at DE. Oxamine orange / G gave a weak band from CÂ ° /, D to b1 /, F, maximum at DÂ° /, E. Oxamine blue MD, weak band in DY, E. Oxamine blue BT, weak band. Oxamine blue BT, weak band from C3, DD DE reachingz OxamÄ ± n: blue DB, strong band from C to DU, E, maximum C to D.

Oxamine heliotrope D, band from C1 /, D to D \ /, E. Oxamine violet GRF, weak band at C? /, D. Oxamine violet MD, two faint bands: at DY, E and C! /, D. Oxamine Violet BBR, drawing two bands from C ' /, D' to D undeyon DE to DB; Maximum bee, Drundâ €™ DDâ €™, EB OxamÄ ± inyiolett GR Is .a very powerful sensitizer, which gives a band from D to E reaching, which has a maximum at D. Oxamine black M, weak band from C! /, D to D. Oxamine black MD, fairly strong band from C to DY, E, maximum C1 /, D. Oxamine black MB, band from C ' /, D to D \*' J, E. Oxamine black BR, two maxima at C? /, D and D1 /, E. The very strong band extends from C to E.

|  
Experiments with color sensitizers on silver bromide gelatin plates. Of  
Paul Ruh.

(Photographic correspondence, 1898, p. 243.)

At the suggestion of the government councilor Dr. J. M. Eder, I examined various color sensitizers with special consideration of the relative sensitivity of the sensitization band in the less frangible part of the spectrum. Larger series of experiments were carried out in order to determine the most favorable and uniformly effective working instructions for the individual dyes.

The starting point was the sensitization of silver bromide gelatine plates with erythrosine, obtained from Schuchardt, which was tried partly with and partly without ammonia prebath. Erythrosine (sodium tetraiodofluorescein) works weaker in a purely aqueous solution than when ammonia is added; cheapest with Ammonia prebath with the following concentrations:

Vonrbad: NMaASSER I a a

ODEAalonlale ze a 2 cm?

The plates are bathed in it for 2 minutes and then in the

Rarbstofibad Wasser a nee 00 KINmonlaler, Se en ne a EZ; BEryÄ ± hrosin solution 1.500722,2222 7 soon

brought during 2 minutes. Then it is dried in the dark. The pre-bath has a very beneficial effect and increases sensitivity significantly. The addition of 2 cm of ammonia? to 100 cm each? Water is to be regarded as the maximum; in addition, there is often a veil.

The plates produced according to the above recipe show high sensitivity and a wide and intensive sensitization band from D to green (DÂ ° /, E); the same is broader and better against Experiments with color sensitizers on silver bromide gelatin plates. 119 Subsequent to blue, as with other types of sensitization. Such erythrosine plates were used as a normal plate for the comparative Spectrum photographs with used the following dyes. An increased addition of erythrosine is not recommended, since the yellow sensitivity remains the same up to a certain limit, but the sensitization band in the yellow-green becomes narrower because the excessive amounts of dye in the layer prevent the access of light according to its absorption and so-called Â Cause «shielding effect».

When overloaded with dye solution, the overall sensitivity is significantly reduced. Adding silvernitrate to the dye bath is not beneficial, as this process impairs the clarity.

An eosin plate made according to the same recipe in eosin solution (tetrabromofluorescein potassium) was 4 times less sensitive than the erythrosin plate in the yellow-green area. The awareness band was also narrower and steeply rising.

Ethyleosin (potassium salt of tetrabromofluorescein ethyl ether) and methyl eosin (potassium salt of tetrabromofluorescein methyl ether), obtained from Monnet & Co., which showed a broader band and a less abrupt maximum, proved to be less effective than ordinary eosin.

The sensitivity of the last two dyes mentioned is also higher than that of common eosin. Since the sensitization maximum of these dyes is almost at the same point as with ordinary eosin (or only slightly further towards yellow), it is advisable to replace the eosin with ethyl or methyl eosin for possible practical work. Rose bengal (tetraiodotetrachlorofluorescein potassium).

The most favorable concentration for this dye (obtained from the Badische Anilin- und Soda factory) is as follows: 2 cm<sup>3</sup> a rose bengal solution 1: 500 per 100 cm<sup>3</sup> Water. A prebath with 2%

ammonia content and an addition of 2% ammonia to the dye bath has a beneficial effect and widening the sensitization band; the same extends from yellow-green to over D into orange, even with the shortest exposure time. The general sensitivity of such plates is reduced by the addition of too high a dye, but even in the most favorable case never reaches that level of erythrosine.

Octiodofluorescein.

Octiodofluorescein shows a band as narrow as eosin, but is more sensitive than the latter. The most beneficial effect is an addition of 2 cm<sup>3</sup> the solution 1: 500 per 100 cm<sup>3</sup> Water and 2% ammonia and indeed no pre-bath is to be used here. Only with a dye addition of 12 cm<sup>3</sup> of the stock solution 1: 500, the prebath had a widening effect on the sensitizing bath, without however, to bring it to the width of the band with the former dye addition.

Phloxin (alkali addition of tetrabromodichlorofluorescein).

Phloxin (obtained from the Badische Anilin- und Sodafabrik) gives bromosilver gelatine plates twice as insensitive as Rose Bengal and four times as insensitive as erythrosin. The position of the sensitization band is almost exactly the same as with eosin (only slightly shifted towards yellow). Does an addition of 6 cm work best? Phloxin solution 1: 500 per 100 cm<sup>3</sup> water and 2 cm<sup>3</sup> Ammonia. A 20% ammonia prebath is beneficial.

The sensitization bath of the phloxin plates is narrow and the sensitivity already drops at an addition of 12 cm<sup>3</sup> Dye solution 1: 500 considerable.

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Bromonaphthofluorescein.

The sensitization band of this dye (obtained from Bayer & Co. in Elberfeld) is even narrower than that of phloxin. Increasing dye content in the sensitizing bath makes the band wider and more intense, but is the same even with the cheapest dye additions of 12 cm<sup>3</sup> the solution 1: 0500 per 100 cm<sup>3</sup> Water and 2% ammonia not satisfactory.

Naphthofluorescein.

A good sensitizer is naphthofluorescein (obtained from Bayer & Co. in Elberfeld), the sensitization band of which has three maxima, the strongest maximum at D, while the two weaker maxima are in orange and against red. The band grows with increasing dye content of the sensitizing bath in terms of width and intensity and the following result was found as the best recipe: |

Vorbad: \ Masseret are RE  
NOREEE Ara oma ee en ee A er  
2 cm?

You soak the drying plate in it for 2 minutes, then let it drain well and bring it into the  
Dye bath: Niassenen u er 9 ON NER Ammonlakerr er. BR En N Nesnlonorse lie 9002  
ee 12rem: The plate is left in it for 2 minutes and then dried. When overloaded with the  
addition of dye (for example 24 cm? Dye solution to 100 cm? Water), the band suffers  
in terms of width. The blue effect is not as strongly depressed as with Rose Bengale or  
Erythrosin, so that when photographing colored objects with a lot of blue the use of a  
darker yellow disc is recommended.

Cyanosine (alkali salt of tetrabromodichlorofluorescein methyl ether).

The sensitization band of this dye it (obtained from Monnet & Co. in N) is pretty good,  
but it is not as wide as the previous one. The best recipe is:

basket bath:

VlaSSerer ta Aa a RE ee. LO FE ammonia.â € œ Br. Ar ee re  
dye bath: MlaSseRe rn Me ON Am Oma a ee a 2  
Eyanosinlosune 0.2 a ee Dibromonitrofluorescein and  
tetranitrofluorescein

are very inferior as sensitizers and not recommended because they, apart from the  
large ones Insensitivity, only give a very narrow band.

Experiments with color sensitizers on silver bromide gelatin  
plates. 122 Monochlorofluorescein, fluorescein, benzylfluorescein.

Monochlorofluorescein gives the silver bromide gelatine plates a continuous  
lengthening of the maximum sensitivity in blue versus green; however, the plates are  
very insensitive. The longest exposure (30 seconds) showed a small maximum at D.  
Fluorescein is also insufficiently effective for dry silver bromide gelatin plates; somewhat  
more sensitive than this the Benzy | - fluorescein, which both give very narrow bands  
and therefore as sensitizers for the practice hardly come into consideration.

Acridine yellow (chlorohydrate of diamidodimethylacridine).

The effect of the acridine yellow (obtained from Leonhardt in MÃ¼hlheim, Hessen)  
shows itself as a continuation of the blue band towards D. But in order to achieve a  
notable success, one is forced to be 30-50 cm? to add an alcoholic, hot, saturated dye  
solution to every 100 cmâ € ™ of water. Thereby the problem arises that the  
photographic plate is colored quite intensely yellow and after fixing the gelatine has to  
be decolored again with alcohol. Pre-bath containing ammonia or the addition of  
ammonia to the dye bath should be avoided as the dye will decompose.

The cheapest recipe for the dye bath should be mentioned:

Mass Wr ee | ee

Alcoholic, hot, saturated acridine gel solution. . 30  
cm? Duration of action 2 minutes.

Chrysaniline (nitrate of diamidophenylacridine).

The effect of chrysaniline (obtained from Schuchardt in Görlitz) is similar to that of  
acridine yellow. It consists in the continuous lengthening of the maximum sensitivity  
in blue against yellow.

Chrysaniline is less sensitive bathing plates than the acridine yellow, but does not color  
the gelatine of the bromide silver dry plates as strongly as this. A warm, saturated  
alcoholic solution

of chrysaniline, of which 2 cm<sup>2</sup> to 100 cm<sup>2</sup> each? Adding water. A stronger addition of the dyesolution causes an inconspicuous widening of the sensitization band, but the overall sensitivity is significantly reduced. The addition of ammonia has a detrimental effect.

Quinoline red.

The position of the sensitization band is similar to that of Rose Bengal, but the latter shows one more intensive sensitization in the orange-yellow. The best recipe is to be considered:

No prebath; Dye bath: water. . re

OWECNLE Quinoline red solution 1:

500. . . 1â€²2 cm<sup>2</sup>

A higher addition of dye reduces the general sensitivity and has no influence on the widening of the sensitization band. The sensitivity of the sensitized area in the yellow-green

is four times less than that of erythrosine,

1622 Paul Ruhr

Nigrosine B.

For Nigrosin 5 (obtained from Bayer & Co.) the best variant of Eckhardt's recipe (see p. 105 of these treatises) turned out to be the one in which there is no alcohol as an after-bath and a pre- bath as well as the actual one Sensitizing bath is added directly. The sensitivity at D was significantly increased, so that not only the maximum in Roth (a), but also the maxima in front of and behind D were fully effective. The recipe is:

Pre-bath: call meers. de eh ethyldalkonol: ern 2 2 un DOM: SAD TE ee a ED

The duration of the pre-bath for silver bromide gelatine plates is 2 minutes. The plate is then placed in the dye bath and left in it for 4 minutes.

Dye bath: NASSCh ea Be a RE WOCHÉ netiylalkponolssiet rare 2 Ainmonlacr Tan ann tere VeNietosmlosung 12900 Er ron

Leaving the panels in this dye bath for too short a time leads to veils and drying streaks. As the addition of alcohol increases, the maximum a becomes more and more intense, while the maximum before D is depressed; in the above recipe, both maxima appear equally strong.

Replacing the ethyl alcohol with methyl alcohol is not recommended, as the sensitivity of the plate is adversely affected.

This concludes the series of dyes I have investigated, the behavior of which at the sensitized point of the photographic plate is given in the following table. It should only be mentioned that with all of these dyes the layer of the plate

You may still touch your fingers while sensitizing, otherwise stains will inevitably appear.

Position of the relative insecurity in the  
medium intensity | horny sensibility  
(opacity) based on erythrocyte = seconds  
throsine = 1



Awareness  
ribbondye

Erythrosin  
eosin     Rose  
bengal

Octoiodofluorescein.  
Phloxin  
Bromonaphtofluorescein  
Napmonluoreseemr 2.27 |  
Experiments with color sensitizers on silver bromide gelatin  
plates.123  
N \_\_\_\_\_

Location of the dye sensitization band  
from to Dibromonitrofluorescein DaB | DEE cyanosine. D BoD 19 Methyleosin DE DEE  
EthyleosinDEE IDEEIE IB. Monochlorofluorescein Blue D '/, E u A ee  
Acridine yellow b G  
Chrysaniline \ an j F quinoline red. J I \ THIEF  
| a B  
Nigrosin BD ED D D D!, E Benzylfluorescein ID ee Fluorescein | DAN E DEE  
TetranitrofluoresceinBe | D DAB

Achieving     a  
medium  
intensity  
do     (opacity)     in  
secondsDD »  
more than Å ± more  
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| Relative sensitivity to  
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The color sensitivity of the various plates was tested by means of the small one Steinheil's spectrographs & vision directe using a constant luminous gas flame (Argand burner) with upstream Bunsen's gas flame, in which saline-containing asbestos was brought so that the yellow sodium line (D) was photographed as the normal line. The different exposure times, which to achieve the same effect on the with the different dyes sensitized silver bromide gelatin dry plates gave an accurate measure of the relative Sensitivity of the sensitized plates.

About new optical sensitizers for silver bromide.  
E. Valenta.

(Photographic correspondence, 1898, p. 314.)

Subsequent to my publication on p. 117 of these treatises, I shall in the following give you the instructions for sensitization which gave me the best results when using oxamine dyes.

Among the dyes of the oxamine group listed on page 117 of these papers, the dyes oxamine red B, oxamine scarlet B and oxamine black BR, especially sea igmaete, are recommended

Water Yan Fe ee SR Pa U 1.00) 000) 02777: Ammonia ur. u rn oe:

let it act for 2 minutes on the silver bromide gelatine plates, whereupon the same in the actual Liche dye bath are brought out, which

NMVassen u ee en ONE Na): <0) ar OS ee ee or Amon ee ee

and the following amounts of dye (in cm<sup>2</sup> of the solution 1: 500): oxamine red B 50 cm<sup>2</sup> ?, respec-tive oxamine scarlet 3 150 cm<sup>2</sup>?, respective oxamine black 80 cm<sup>2</sup> .

The plate remains in the bath for 4 minutes and this should be kept moving during this time. Then it is taken out, rinsed in a second bath of the same type, and left to dry.

It goes without saying that this work must be carried out completely in the dark and that the use of red light is also excluded, since even with Oxaminroth B the sensitization reaches up to C, so the orange-red rays have an effect.

In the following I give a discussion of the effect of a number of other dyes of various origins that I have examined, which dyes of the k. k. Graphic teaching and research institute made available

in a lovable way by the companies concerned. I want to start with two dyes which gave particularly useful results.

It is primarily a dye from Farbwerke formerly F. Bayer in Elberfeld, the diazo black BHN. About new optical sensitizers for silver bromide. 195

The same gives using the ammonia pre-bath above and 80 cm? Dye solution 1: 500 by 700 cm? Water, 200 cm? Alcohol and 10 cm? Ammonia as a dye bath in compliance with the previously described process. Plates, which provide a very strong band from B to D', E, the maximum of which is at C' /, D. A comparison with nigrosine 3) from the same factory, which was found in tests on the k. k. Graphischen Lehr- und Versuchsanstalt has proven so well as a red sensitizer, showed that diazo black BHN Amal is as sensitive in red as this dye.

Even greater sensitivity with greater power of sensitization can be achieved with the benzonitrole brown marketed by the same company.

This dye, used in the same way as the diazo black for the preparation of drying plates, gives a broad sensitization band from C! /, D to over E with the maximum D' /, E. It does not extend so far into the red part of the Spectrum beyond that of diazo black and nigrosine, but wide enough for taking pictures of paintings as it is relatively very sensitive to the orange-red and yellow rays (6 times as sensitive as nigrosine).

These two dyes, of which the diazo black BHN is undoubtedly the most useful red sensitizer known to date, I include the other examined dyes, sorted according to the companies that produce them. Among them are dyes which deserve a high degree of attention and which are very useful, especially for spectral recordings should prove.

Dyes from Dahl in Barmen.

Alkali dark brown. Band ranging from C to D with a maximum C' /, D.

Alkaline red brown GR. Band from C to E, maximum at D strong. Best concentration 1: 500 to 100 cm? Water and 2 cm? Ammonia.

Alkaline garnet gives a strong band, from B to E, with a maximum at D. Best concentration 10 cm? the solution 1: 500 to 100 cm? Water and 2 cm? Ammonia.

Alkali dark brown V shows two maxima, at C' /, D and D' /, E, and gives a rather strong effect between C and D.

Dyes from Meister, Lucius and Brünning in Höchst a. M.

Dianile black G gives a strong band, from C! /, D to D' /, E, with a maximum lying at D. The best concentration is 3 cm? the solution 1: 500 to 100 cm? Water and 2 cm? Ammonia. An ammonia prebath is beneficial.

Dianilschwarz R gives a strong band with a longer exposure, reaching from C to E, which reveals two maxima, one at C' /, D and a second, faded, after D. When using the method described at the beginning with a pre-bath using 5 cm? Dye solution every 100 cm? Dye bath plates are obtained which exceed those with nigrosine preparation in terms of sensitivity in the red 4 times.

Dianil blue B, two faint bands at C' /, D and D' /, E.

Dianil blue 2R has a weak effect. Band from C! /, D to D' /, D, maximum C1 /, D. Another narrower band is Dianilblau R.

The dyes gave very weak sensitization bands: Chromotrop SD, maximum at D' /, E; Chromotrop 6B and Janus brown, maximum at E! /, D to D' /, E; Janus blue, maximum

at  $B\lambda^\circ \lambda^\circ /$ , C to D, while Janus green was veiled.

1) cf. P. Ruh: "Experiments with color sensitizers", p. 118 of these papers. une BE

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Dyes from Kalle in Bieberich a. Rh.

The naphthylamine blue proved to be powerful sensitizers for the red and orange-yellow rays from 5 to above D, namely naphthylamine blue 25 and 2 give a strong band, ranging from Cr to 4P, -Naphthylamine blue 5A a very strong: band, ven Ba, @ pie 72 (maximum C  $\lambda^\circ /$ , D) and a similar one from D  $\lambda^\circ /$ , E to D  $\lambda^\circ /$ , E (maximum D, E). Naphthylamine blue 3R, band from C to D (maximum C  $\lambda^\circ /$ , D). The best concentration for these dyes is 6cm? the solution 1: 500 to 100 cm? Water and 2cm? Ammonia. Pre-bath with 2% ammonia works well.

Tolaniroth sensitizes DY, C to D  $\lambda^\circ /$ , E. The effect is: weak; this. In an aqueous solution, dye gives strong absorption bands, even when very diluted. The absorption ranges from D to violet; it would therefore be beneficial to use in making color filters.

Walk blue gives a strong band from C  $\lambda^\circ /$ , D to D (maximum C?) With a higher concentration (- 10 cm? Of the solution 1: 500 per 100 cm? Water and 2 cm?  $\lambda^\circ /$ , D), but causes fogging.

Dyes from The Clayton Aniline Comp. Limited ».

Curcuphenin Yellow, Chlorophenin OR, Rosophenin  $\lambda^\circ$  4B, and Nitrophenin gave weak sensitization bands; Rosophenin 4B, which had two bands, a stronger band from D to E (maximum D  $\lambda^\circ /$ , E) and a weaker band from D to D that only appeared with longer exposure, had the strongest effect  $\lambda^\circ /$ , C with the maximum at D.

Dyes from the color works Leopold Uassella in Frankfurt a. M.

Diaminreinblau FF gives a weak band from BE NCHbEE = DENE Diamineral blue has a strong effect, bands from C  $\lambda^\circ /$ , D to D and before D to DU, E - - Diamintielschwarz (r) there are two bands, 5, C-bis Daund pe "DAN, RB, the leiztereis weak and only emerges after a long exposure. Has a strong effect.

The diamine yellow and diamine pink dyes hardly work at all, and diamine orange only gives a hint of a maximum in D after prolonged exposure.

Cyanol extra gives in a dilution of 1 cm? (1: 500) on 100 cm? Water, 2 cm? Ammonia and 0: 5 cm? Silver nitrate solution (1: 1000) a narrow, weak band at D against a, furthermore a broad, weak band at B  $\lambda^\circ /$ , C and a band at DV, E

Neuphosphine G gives only a weak band between D  $\lambda^\circ$  and E, even in fairly strong concentrations. Lanacyl blue 55 and Lanacyl violet, narrow band at B, wider band at C (Concentration 1  $\lambda^\circ$  "2 cm? Dye solution 1: 500, 100 cm? Water, 2 cm? Ammonia).

Of a larger number of newer tar dyes, the production of which is operated by the "Badische Anilin- und Sodafabriken", the silver bromide gelatine plates were found to be able to sensitize: Iris blue, after Schultz?) The ammonia salt of Tetrabromresorufin, there are two narrow but strong bands at C and at C  $\lambda^\circ /$ , D

1) Is a triazo dye of the diamine black group. The dyes in this group are mostly sensitizers. Concentration: 2 cm? Dye solution 1: 500, 2 cm? Ammonia and 2% ammonia prebath. 2) "Tabular overview of the artificial organic dyes available on the market", Berlin 1897.

About new optical sensitizers for silver bromide. 127

Anthracene blue SW.X gives in concentrations of 2â € "4 cm? on 100 cm? Water and 1 cm? Ammonia with longer exposure weak continuous effect reaching beyond 5.

Woolen print blue gives a narrow band from C to D? /, E. Maximum C /, E.

Anthracene blue WGG in dough form, 6cm? the solution (2'5: 500), 2cm? Ammonia, strongband, reaching from B /, C to over D.

Naphthyl blue 2B (product from o-amidodiphenic acid) showed a weak band between D and E(maximum D \, E).

Alizarin black. Weak band between C and D, maximum C1 /, D; the blue becomes at concentrations of 10 cm? on 100 cm? Water and 2 cm? Ammonia already strongly depressed; greater concentration causes fogging.

Cotton black B gives powerful effects even with low concentrations; at 3 to 4cm? on 100 cm? Water and 2 cm? Ammonia gives you a strong band from B to CÂ ° /, D, maximum CY, D. An ammonia prebath is beneficial.

Diazo Black 3B is a benzidine dye; it already works in dilutions of 0'5 cm? on 100 cm? Water and 2 cm? Ammonia as a powerful sensitizer. The effect ranges from B to DÂ ° /, E (with longer exposure), maximum C1 /, D.

Palatine Black 4B acts as a sensitizer for the red rays of the spectrum; with longer exposure there is a strong band, ranging from A to D (maxima at a and 5).

Dyes from the Farbwerke formerly Fr. Bayer in Elberfeld.

Azogrenadine; weak band from D \, E to DÂ ° /, E; Maximum D /, E.

Double ponceau R, 2R and 3R give very weak bands from CÂ °? /, D to D! /, E, maximum DY, E. | Dolphin blue (according to Schultz, a product made from gallocyanine chlorohydrate with aniline) has a very weak sensitizing effect and gives a band from C to CÂ ° /, D, maximum C1 /, D.

|

Sulphonic acid blue gives two bands, one from D \, E to DÂ® /, E and a very narrow one with the maximum D \, C. |

The alizarin dyes: alizarin viridine and alizarin cyanine green ZÂ £ have a sensitizing effect on the red rays of light. The former dye strongly sensitizes from B to C1 /, D, maximum atir @; the latter, sings faded bands at DIE and 'at D against: D.

Oxamine blue 3R, which has a well-defined band of C 6152925, 5, maximum 02, D, has a strong sensitizing effect.

The different acid violet, namely R, 2R, 3R, 4BG, sensitize for the orange-red part of the spectrum.

Acid violet RR and RRR work best. The bands are very strong and extend from 01, Drpis & 2 /, D- with longer exposure to DD "; E reiehend), maximum CÂ ° 7, Dec. Best concentration: 10 cm? To 100 cm? water and 2 cm? ammonia.

Benzonitrold dark brown has a very strong effect in the orange-yellow, yellow, and yellow-green parts of the spectrum; the sensitization band extends from C1 /, D to over DÂ ° Â® /, E with a maximum at DR.

New toluene brown also works well. The best effect was achieved with the M brand. It gives a strong sensitization in the red and yellow-red part of the spectrum. There were two maxima, namely at C! /, D (strong band, reaching from B to D) and at D! /, E (a narrow, weak band). The overall sensitivity of the plates is little depressed.

128 Å © E. Valenta, on new optical sensitizers for silver bromide.

From Å® black? Dyes became phenolic black. Diazo black BZN and ZP / RU to black examined. Pluto black B has almost no effect; Pluto black G, on the other hand, gives a very strong band from B to D Å ° Å® /, E with the two maxims CY, D and D \, E. Pluto black R also has a very strong effect and, using the instructions given at the beginning, gives 5 cm? Dye solution 1: 500 per 100 cm? Bad Amal plates as sensitive as Nigrosin B. The band from B to D Å ° Å® /, E with the two maxims C ' /, D and DJ, E stands out sharply and this dye should gain practical importance. |

Phenolic black gave unsatisfactory results; with this dye there is a weak band, from DY, E to D Å ° Å® /, E, and a weak continuous effect, to. Reaching beyond a becomes noticeable with longer exposure. In practice, those dyes that are not strong, show rapidly swelling maximum, worthless from the start.

The sacchareine as sensitizers for silver bromide gelatine plates. Of

E. Valenta.

(Photographic correspondence, 1899, p. 30.)

P. Monnet and J. Koetchet!) Made the observation. that saccharin (benzo & acid sulfimide), which is often used as a sweetener instead of cane sugar, is formed with phenols and amidophenols of compounds, which show a great similarity with the phthaleins, reacts. The reaction with phenols is given by the equation:

a En H, OH ES | C, H, OH CHC NEE nor golc Å ± l nd Nso 7 | â € so e

expressed. The bodies produced by the reaction with phenols are called saccharine.

Analogously to the cleavage of saccharine into o-sulfo benzoic acid and ammonia, the saccharine is converted into the corresponding sulfurine and ammonia. split: Å „EREI ZONE a l CE ORT

SE> 00 | <= o 2267 H. OR | E20. . OL Å © BL NH + H, 0 = (C, ax y9 + NH, 30; | SO, resorcinol

saccharein | sulfurein

The derivatives of m-amidophenol, which belong to this series, are very similar to rhodamine in terms of color strength and general properties.

Since various phthalein dyes are known to be very good optical sensitizers for bromosilver, the assumption was made that the saccharein dyes found by P. Monnet and J. Koetchet would also emit useful sensitizers. .

Mr. P. Monnet had the kindness to answer the request of the k. k. Graphischen Lehr- und Versuchsanstalt to put small samples of such dyes at the disposal and were the ones with very satisfactory for the same results obtained.

1) "Chemisches Centralblatt", 1897, II. Th., Pag. 521, from: Bull. Soc. chim., Paris, (3rd) vol. XVII, pag. 609 to 702. 1

130 E. Valenta: The sacchareine as sensitizers for silver bromide gelatine plates. The behavior of the following dyes was examined:

I. saccharoeosin (saccharein des tetrabromoresorcinol). The saccharoeosin is a brown-red powder which is somewhat difficult to dissolve in water and alcohol, easily in solutions of alkalis

with a carmin-red color with the appearance of a green-yellow fluorescence and very easily in the ether with a red-yellow color and less fluorescence.

The solution has a weakly alkaline reaction.

When hydrochloric acid is added, the red aqueous solution turns yellow and the fluorescence disappears; Adding excess ammonia restores the old relationship. The dye is completely insoluble in benzene. |

2. Diethyl m-amidophenol saccharein (chlorohydrate). This compound forms a metallic, green, glossy powder which is insoluble in water, but easily dissolves in alcohol with a neurotic color; the solution fluoresces a glorious blood red. Alkalis and ammonia destroy the color immediately. The dye is completely insoluble in ether and benzene.

2. The acetylated product of the Sacchareines-pictures written in sub 2 is a pure violet powder with greenish metallic reflections. It is soluble in water, alcohol, alkalis, ammonia with a violet-red color and very lively blood-red fluorescence, which is particularly pronounced when it is very diluted. The addition of hydrochloric acid changes the color of the aqueous solution and makes the fluorescence phenomena disappear. It's pretty difficult to dissolve in aether with red-yellow fluorescence, insoluble in benzene. | |

4. Sulfurein of diethyl-m-amidophenol (sulfate), violet-brown powder with green metal reflex. Easily soluble in water and alcohol with a deep red color. These solutions, but even more so those in ammonia, fluoresce very intensely blood-red.

Hydrochloric acid makes the fluorescence phenomena disappear. In ether the dye is difficult to dissolve with neurotic color and yellowish-red fluorescence; it is insoluble in benzene.

The sensitization experiments described below were carried out with the following dye baths. For dyes no. 1, 3 and 4 pre-bath: water 800 cm<sup>3</sup>, Alcohol 200 cm<sup>3</sup>, Ammonia 15 cm<sup>3</sup>. Dye bath: water 800 cm<sup>3</sup>, Alcohol 200 cm<sup>3</sup>, Dye solution (1: 500) 100 cm<sup>3</sup> and ammonia 15 cm<sup>3</sup>. No prebath was used for dye # 2 and the ammonia-free dye bath above was used.

All of these dyes worked very well. Sucroseosine produced a strong band from D to D<sup>\*</sup>, E, with a maximum at D<sup>1</sup>, E.

Dye No. 2 gave two bands: a narrower one, the maximum of which is at D, and a wider, much weaker one, with the maximum D<sup>2</sup>, E.

Dye no. 3 showed a strong band from C<sup>2</sup>, D to D<sup>1</sup>, E (maximum C<sup>1</sup>, D) and a second faint band at D<sup>2</sup>, E on prolonged exposure. |

The effect was very favorable when using the sulfurein of the diethyl-m-amidophenol. It appeared as a strong band from C<sup>1</sup>, D to D<sup>1</sup>, E reaching the maximum at D and a second, weaker, but broader band with the maximum at D<sup>2</sup>, E, which almost completely fills the gap up to above E with a longer exposure. |

The dyes have the advantage that the gelatine easily releases them into the washing water when the plates are washed out. The saccharein of diethyl-m-amidophenol can also be easily destroyed by alkalis, so it can easily be removed from the layer even with the use of more concentrated dye baths. If you add some ammonia to the first wash, what

may be desirable under certain circumstances.

Investigation of some tar dyes for their ability to sensitize them to bromide silver. Of

E. Valenta.

(Photographic correspondence, 1899, p. 336.)

The management of the Baden aniline and soda factories in Ludwigshafen a. At the instigation of Mr. Commerzialrathes Glässer, Rh. Was so gracious to provide us with 97 dyes from the laboratory (pure products) for test purposes.

The dyes were tested for their ability to sensitize bromide silver in gelatine and collodion emulsions, and dry plates from Fitma'schleussner on the one hand and Collodion emulsion plates (bromzinc-collodion) on the other hand were used for the stated purpose. The latter plates were prepared in such a way that the plates were poured with the colored emulsion and bathed in a silver bath with the usual concentration before exposure.

The exposition was carried out by means of the little Steinheil's spectrograph in the same way as I have described in detail in my publications on this subject (see "Photographische Correspondence", 1897, p. 129). (5. of these treatises, p. 109.)

Phenamine blue Downhill on silver bromide gelatine plates only after longer exposure a weak band from C to D reaching; Phenamine blue G behaves in a similar way, while phenamine blue \$R has no effect. left. | |

As already known, ethyl violet acts as a useful sensitizer; There are two bands on gelatine plates, the first of which is strong and extends from C to D with the maximum C' /, D, while the second, weaker one, only with longer exposure at D' /, E emerges. The effect of this dye on Collodion emulsion plates is also very strong. If you add about 1 Å ° /, alcoholic dye solution 1: 150 to the Collodion emulsion, you get a strong band with the plates sensitized in the silver bath (2: 1000), which were cast with this emulsion ranging from B' /, C to C' /, D, with the maximum at C' /, D and a second weaker band with the maximum DAB. The effect in orange and red significantly exceeds that in blue. With a long exposure, a third band appears, which lies between A and a and is very faint.

Alkali violet extra?) Gives a strong band from C to C' /, D on gelatine plates, with the maximum at C' /, D; it also works on collodion emulsion and gives a strong band of

Ä ±) Hydrochloride of hexaethyl pararosaniline. Schultz: "Tabular overview of artificial organic dyes", 1897 pag. 110. 2) Sodium salt of tetraethylmonomethylphenylpararosaniline sulfonic acid.

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5 to C' /, D, next to which there are two narrow, weaker bands between D and F (with -D' /, E and 2' /, F).

Acid Violet 4 R had no effect with gelatin plates. On the other hand, it turned out to be a powerful sensitizer to Collodion plates. One obtains a broad band from C over E with the maximum at D.

The tetramethylphenylpararosaniline (chlorohydrate) had a strong effect. The same gave a band ranging from C to C' /, D, maximum with bromosilver gelatin dry plates. 1), Dyauchâ € the tetramethyldibenzylpararosaniline had a strong effect; on the other hand above bentamethylphenylpararosaniline no picture. The sensitivity of the plates is strongly depressed. The behavior of the first dye on Collodion emulsion plates is interesting. In the presence of larger amounts of dye in the emulsion (1cmÂ® dye solution 1: 150 on 20cm?) A band from B to U, D emerges very strongly; with increasing dilution, a second band, which extends from D to F



and, in the case of: bromosilver gelatine plates, can only be detected after a very long exposure, becomes stronger and stronger; at 1:80 (emulsion) it is five to six times as strong as the first tape. This band has two maxima at DY /, E and 5b! /, F, the first of which is particularly strong.

Pentamethylphenylpararosaniline (chlorohydrate) also has a strong effect on Collodion emulsion plates; you get a band from  $\hat{a}, \neg$  to 5 with two maxima, the first of which is at Car sgeleseniner while the second, weaker one is at  $\hat{D} \hat{A}^{\circ}$  /, E.

Triethyltriphenylpararosaniline (chlorohydrate) gave almost no effect on gelatine plates, and a fairly good effect on colodion plates. The band extends from B to C2 /, D:- maximum CD).

The tetramethyldiphenylpararosaniline (chlorohydrate) formed an indistinct, faded band between D and E on gelatine plates; In the case of Collodion emulsions, there is a strong band from B to  $\hat{C} \hat{A}^{\circ}$  /, D and this is followed by the faded, indistinct band.

The sodium salt of the sulfonic acid of the triphenylmethane dye from o-chlorobenzaldehyde and ethylbenzylaniline gave a weak, narrow band between B and C, a similar one for C1,,: D, and, with long exposure, a third for A. The sodium salt of the sulfonic acid of triphenyl methane dye from trichlorobenzaldehyde and methylbenzylaniline produced a band from C to D reaching. | Three types of indulins were examined. |

$\hat{A} \in \text{œ Indulin reddish tinge} \hat{A} \in$ , soluble in gas, had a worse effect than the ammonia salt of the sulphonic acid, which produced a tape with the maximum at D on gelatine plates without being strong, while it was strong for collodion plates Represents sensitizer. A strong band is obtained from D to E with the maximum DY, E, which is followed by a second band extending to over F after a longer exposure. |

The types C, WG, G and M of nigrosines were examined, of which only the WG brand worked well on gelatine plates. A strong band with the maximum between a and B and a much weaker band with the maximum at C /, D and, with a very long exposure, a third narrow band at A was obtained. Nigrosine WG demands a great initial effect of the light. Two nigrosin varieties examined later, W extra and F, gave three bands (A to a, C! /, D and DY, E).

In the case of Collodion emulsions, the effect of Nigrosin WG is far more powerful and ranges from k = 800 to X = 980, whereby the blue effect had not yet come to the fore. | The three types of nigrosin that work well are sulphonic acids, and the WG brand is that of a nigrosin produced by the Baden aniline and soda factories using a secret process, as the factory mentioned informs us. =

Dimethylsafranine, made from dimethyl-para-phenylenediamine, orthotoluidine and aniline chlorohydrate, works

not at all on gelatine drying plates; with Collodion records you get a band from a to  $\hat{a}, \neg$ ? /, D Investigation of some tar dyes for their ability to sensitize them to bromide silver. 99 sufficient, with the maximum at C! /, D. The plates are very insensitive. The tetraethylphenosafranine (from diethylparaphenylenediamine, dietylaniline and aniline chlorohydrate) is so slow that no image was obtained with the normal exposure times.

Sulfanils.  $\hat{a} \in$  "azo | an Ya x, -amido-a, -naphtol-2, -sulfonic acid is a powerful sensitizer for both silver bromide gelatine and collodion plates. A band from C to  $\hat{C}^{\circ}$  /, D with the maximum C! /, D in the case of gelatine plates is obtained. In the case of Collodione emulsions, if the exposure was sufficient, the band extends from A closed to D /, E with the maximum  $\hat{a} \in$  at C. The analogous m-nitroaniline compound:

Sulfanils.  $\lambda \in \text{''420 Ns } \hat{A} \odot \text{ ee y}$ , -amido-a, -naphtol-x, -sulfonic acid had no effect when strongly diluted, and when using stronger concentrations total haze.

While o-amidophenol-p-sulfonic acid-azo-a-naphthylamine-azo-z, -naphtol-a, -sulfonic acid for gelatine plates has two volumes, namely a to C (maximum B) and  $C \hat{A}^\circ /$ , D to  $D \hat{A}^\circ \text{ ''}$  /, E (maximum D), I received no sensitization with the nitro-o-amidophenol-p-sulfonic acid-azo-x- naphthylamine-azo - @ - naphthylamine.

Likewise, another such nitro compound was that: Nitro-p-amidophenol-o-sulfonic acid-(Bs] zaey. Ee with no effect. 174

A third nitro compound: nitro-o-amidophenol-o-sulfonic acid-azo-2-naphthylamine-azo-a, - naphtol-z, -sulfonic acid again had a strong effect: band from 025.  $D^*$  to:  $D_2$  , 2,  $\text{Max} \hat{A} \pm \text{mumAt}$ : |

While benzidine-disazo- $\hat{A} \in \text{œ}$ , -amido-a, -naphtol- \$, - sulfonic acid did not work at all, dianisidine-disazo- $\beta$ , -amido-x, -naphtol- $\beta$ , -sulfos $\hat{A}$  Gelatin dry plates very strong from B to  $C^* /$ , D and somewhat weaker from D to  $D \hat{A}^\circ /$ , E.

There was no effect when using Bezidin-sulfosäure-disazo- $\beta$ , - amido-o.-naphtol- $\beta$ , -sulfonic acid. 3 4

(&)

$\hat{A} \pm$  sulfonic acid) 183

and the hydrol blue from: tetramethyl-diamidobenzhydrol +0,  $\beta$ , -dioxynaphtalin- $\hat{A}^\circ$ , - sulfonic acid

The sulphonic acid de s Nilbiau (nitrosodiethyl-m-amidophenol +  $\hat{A}^\circ$  «, -naphtylamine a band between C and D; in the latter compound the maximum was  $C^* /$ , D and the effect in both was weak. With hydrol blue, Collodion emulsions were strongly veiled plates received.

About sensitizing the silver bromide gelatine plates for the Lippmann Process. Of

E. Valenta.

(Photographic correspondence, 1899, p. 539.)

It is a well-known fact that, particularly when using thin layers of bromosilver gelatin to produce images in natural colors, the exposure must be met exactly if the reproduction of the mixed colors is to be reasonably good. This is to a certain extent connected with the color sensitization, as I had the opportunity to convince myself through a series of experiments which I made in the direction mentioned. The greater the difference in the sensitivity of the bromide silver to the main colors of the spectrum, red, yellow and blue, the more difficult it is. It will be more difficult to find the exposure time that gives the best color effect. The ideal would be a real panchromatical cal plate, that is, a plate which is equally sensitive to all colors of the spectrum. | Unfortunately we still do not have such a plate today and so we have to try to come as close as possible to the ideal of the panchromatic plate by choosing the appropriate sensitizer. | |

So far, most regulations for the sensitization of silver bromide gelatine plates for the Lippmann process contain cyanine or mixtures of cyanine with quinoline red (Lippmann!), 1899), cyanine and erythrosine (Krone?) And others useful sensitizer for the orange-yellow rays, while yellow- green and green-blue remain behind and the effect in blue exceeds that in yellow-red many times. An addition of quinoline red removes the former deficiency, an addition of erythrosine

causes the opposite relationship between red yellow and green. It is therefore a matter of finding a dye which has a uniform and strong effect from red, or orange-red to blue-green and, if the blue effect should nevertheless be a bit too strong, allows it by simply switching on a weak yellow filter to achieve the same effect in blue.

If a dye is to meet these requirements, it must have a very broad and at the same time fairly strong band of (C against E. Good sensitizers with extremely narrow bands, which are always preferred for the purposes of recording for three-color printing, work unfavorably here .

For example, according to my experiments, glycine red, which was developed by Kinzelberg: ae

2), B&#147;lleesoex Rranes 1899:?) Representation of natural color through photography, Weimar 1894, p. 68.

About sensitizing the silver bromide gelatine plates for the Lippmann Process. 135 is placed on the market. This dye gives a sensitization band almost as strong in green as in blue. The same goes from A /, C to over 5b and the sensitivity of the plate sensitized with it is quite large.

The glycine red, in the amount of 12 to 14 cm<sup>3</sup> (1: 500) per 100 cm<sup>3</sup> added to the emulsion described in my book: "Photography in natural colors"), gave me very good results in that both the Main colors as well as very delicate nuances are clearly reproduced.

At the end of this article, I would like to say that Lippmann has recently been producing his emulsion by adding finely powdered silver nitrate to a solution of gelatine, water and potassiumbromide.

In this way, emulsions are obtained which provide very clear images and have a very fine grain. With such emulsions I made comparative experiments with the emulsion I described at the time (a. A. O&#221;--), But could not find any advantage of this method over the one I described.

1) 1895, Knapp, Halle a. S., p. 52. S. also «Photogr. Chemistry », 1899, p. 108.

Investigation of tar dyes on their ability to sensitize them to bromide silver. Of

E. Valenta.

(Photographic correspondence, 1900, p. 99.)

In the same way as I have already described in previous publications!) On this subject, a further number of tar dyes were tested for their sensitizing power. |

It should only be noted at this point that for these experiments bromosilver gelatine drying plates with a sensitivity = 10<sup>4</sup>  $\circ$  Scheiner were used, furthermore that the concentration of the dye solutions for drying plates 1: 25,000 to 1: 50,000, and their ammonia content 1 to 2<sup>4</sup>  $\circ$ ). For the experiments with collodion emulsion plates, a bromine zinc collodion emulsion was used, which was colored with an alcoholic solution of the dye in question. The latter plates were soaked in a silver bath of the usual concentration before exposure.

The following dyes were examined:

Dyes from the Farbwerke formerly Fr. Bayer in Elberfeld.

Benzoroth SG gives a strong band from B to D<sup>4</sup>  $\circ$  /, E, with the maxims OD) Use D'J; E.

Tronaroeth 3B and Tronaviolet B act as weak sensitizers on silver bromide gelatine plates. The former dye gives a faint band ranging from C \ /, D to DÂ® /, E, maximum at D; the latter dye has the same band from D! /, E to E with the maximum at DV, E  
 Pluto orange G sensitizes from D to C (with longer exposure); Maximum YORE  
 Pluto brown. Several brands were examined. These dyes mostly gave poor results on bromosilver gelatine dry plates. In contrast, the brands NB, GG and R work favorably on Collodion emulsion; with longer exposures a closed band from a to over EZ is achieved, so that when using a weak Yellow disc almost perfect conclusion from A to A can be achieved. The maxima, of which there are two for dye GG, for D and for E, are indistinct and difficult to see.

Pluto brown R gives a band from C to D! /, E, the blue

') "Photographic correspondence", 1899, p. 336 and these treatises, p. 131.

Investigation of tar dyes on their ability to sensitize them to bromide silver. 137

effect is strongly suppressed by this dye; it is less than the action of yellow and red parts of the spectrum.

Azo acid blue 63 has a sensitizing effect on collodion emulsion plates. Band from A! /, A to D \ /, E maximum at C ' /, D

Victoriaviolet 4 BS gives a band from B to DÂ° /, E with Collodion emulsion, maximum with EI5D

In the case of silver bromide gelatine plates, wool blue N gives a narrow but strong band in the case of C.

Diazoindigo blue M colors neutral bromide silver intensely. There is a band going from A to E with longer exposure. The blue effect is strongly depressed.

Benzodarkgreen GG does not sensitize bromosilver gelatine, Collodion emulsion plates quite strongly. With shorter exposures there is a narrow band, reaching from A to B, with longer exposure an almost closed spectrum from A to H.

Pluto black BS extra gives a strong band from a to D with a longer exposure, with a maximum at

C. Pluto black FR gives a band from A to D \ /, E, with a maximum at B. | |

Diamond black FR, with longer exposure a strong band, reaching from A to towards D, maximum at B \ /, C |

Direct blue black 2B, band from a to DY, E, weak with short exposure; only for longer exposure, two maxima, B! /, C and D \*! J, E, appear blurred.

Dyes from the company for aniline production.

Guynea Violet 4B. Has a strong effect on silver-bromide gelatine plates, but causes a strong red veil to develop; Band from C to DÂ® /, E, with two maxima at C ' /, D and D \ /, E, the former of which is strong.

Guynea green B extra. With a longer exposure, a fairly strong, very narrow band occurs at @ 1, D aut. |

Without the addition of ammonia, leaf green results in a narrow band that is only strong when exposed for a long period of time, from B! /, C to C ' /, D, maximum behind C.

Ethyl green, crystallized. Has a sensitizing effect on silver-bromide gelatine drying plates and gives a narrow, sharp band from BYJ, C to. CD

Mandarin G extra and RL. The former of these yellow-red azo dyes is the sodium salt of sulfanilic acid azo- $\beta$ -naphthol; it acts on bromide-silver gelatine drying plates and gives a broad band from a to D with longer exposures, in which two maxima can be seen at B and at C1 /, D. Even with a

short exposure, the dye RL gives a fairly strong band in yellow-red ranging from C to D, with the maximum C  $\frac{1}{2}$ , D; In addition, a blurred band between D and E occurs with a very long exposure. From two brands of Echtbraun, Echtbraun 3B already looks strong with a short exposure. Band from C  $\frac{1}{2}$ , D to D  $\frac{1}{2}$ , E, maximum C  $\frac{1}{2}$ , D; with a longer exposure a second, narrow band appears with the maximum B  $\frac{1}{2}$ , C and with a very long exposure a third between D and E, so that the band then seems to extend from a to almost E, as all three into one another blur. In the case of brand G, only the third band appears and only after a longer exposure.

Real blue R (for wool) is the sodium salt of the sulphonic acid of a product of indulin melt (Georgievics).

As a sensitizer, it behaves very similarly to the nigrosines in that there are three bands, namely a very strong one, ranging from C  $\frac{1}{2}$ , D to C  $\frac{3}{4}$ , D, which emerges with a short exposure, then

a weaker one from a to D, finally a third from D to D  $\frac{1}{2}$ , E. The maxima of these bands are 18 138 E. Valenta, investigation of tar dyes on their ability to sensitize them to bromide silver.

at 5 $\times$ 2, D, a $\frac{1}{2}$ , B and D  $\frac{3}{4}$ , E. If the concentration of the bath solution is somewhat stronger, Roth veil appears.

Wool black 4B is a very powerful sensitizer that has a powerful effect even with a short exposure. In this case, you already get a broad band from A to over D, with an indistinct maximum at 3. With longer exposure, a second blurred band from D to almost E is added, the maximum of which could not be determined. This dye suppresses the blue effect somewhat and, since the blue effect only slightly surpasses those in red and yellow, should be very useful for practical purposes.

Of two brands of Columbiaschwarz, brand B produced a strong band on longer exposure, extending from a to C  $\frac{1}{2}$ , D, with the maximum at C. The dye gave the bromide silver plates a strong red haze.

Organic, 21,

A-BC = D TER MARRIAGE (7 h lat

Spectrum photograph on silver bromide gelatin with a) formyl violet, b) wool black 4B.

Formyl violet 5, 4B v is a very good sensitizer, which has a strong effect even with very short exposure on Cassella in Frankfurt a. M. This dye is identical to Acid Violet 6B from R. Geigy in Basel and Acid Violet 4B extra from Ms. Bayer in Elberfeld (€). It is the acidic sodium salt of tetraethyldibenzylpararosanilinedisulfonic acid and forms a blue-violet powder, which easily dissolves in water with a blue-violet color. The aqueous solution stains neutral bromide silver

slightly. At a dilution of 1: 50,000 with 1 to 2 °, ammonia used as bathing liquid, the dye gives a strong band from C to D, with a clear maximum at C  $\frac{1}{2}$ , D. With longer exposure, a second one, reaching from D to D  $\frac{1}{2}$ , E, is added, so that the sensitization band extends from C to almost E with long exposure, whereby it is not much inferior to the blue effect in terms of strength.

1) G. Schulz: "Tabular overview of artificial organic dyes", 1897, p. 116. Investigation of tar dyes on their ability to sensitize them to bromide silver. Of

E. Valenta.

("Photographic Correspondenz", 1901, p. 231 and 490.)

Since my last publication in this field!) I have read a number of dyes, some of which have been known for a long time and some that have only recently come on the market, with regard to their sensitizing ability for bromosilver gelatine and bromosilver collodion emulsions.

sions checked; the procedure described earlier?) was used for this test. Dyes from the Farbwerke formerly Fr. Bayer in Elberfeld.

Alizarin pure blue B, powder, gives a rather strong, sharply defined band from B to C! /, D with the maximum at C.

Alizarin blue black 3B, powder, looks quite strong on drying plates; In the case of medium exposure, two bands appear with the not sharply protruding maxima at B and at BJ), C, to which a blurred band between C and D occurs with longer exposure.

Benzoechtblau BN patented, furthermore Benzoechtroth Z patented, BenzoechÄ ± scehal lach GS and Rhodulin heliotrope gave no result.

Benzobraun RC causes a broad, indistinct band from B to over D to appear on silver bromide gelatine drying plates after prolonged exposure; In the case of Collodion plates, an indistinct band from D to E appears after a longer exposure.

Benzobraun D3G extra has almost no effect on drying boards; with Collodion emulsion there is a band from C to D, which only becomes more pronounced after a longer exposure time.

Benzochrome brown 5G only gives a faded band on DJ, E after a longer exposure.

The effect appears to run almost continuously from F to C.

Benzoolive only gives two faded bands with long exposure, the indistinct maxima of which are at A and C', D. |

1) cf. 136 of these treatises. 2) "Photographische Correspondenz", 1897, p. 129 and 185; also these treatises, p. 109.

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Benzodark green B is also a very moderate sensitizer; a band from BD to C only appears after longer exposure.

Benzo green G gives a weak band with the maximum B1 /, C in Collodion emulsions.

Thiazole yellow is a coloring agent with an excellent effect, especially in the case of Collodion emulsions. This dye belongs to the group of diazoamido dyes and has been known since 1887. In an alcoholic concentrated solution it gives the emulsion, after silvering the plates, layers of high sensitivity to yellow and green, which on prolonged exposure give a broad,

Fig. 22,

ABC D Eb F G h HH,

AsBE DER - E G h HH,

1. Thiazole yellow (dry plate). â € "2. Thiazole yellow (Collodion emulsion). â € "3. Nitrophenine yellow (dry plate). â € "4. Nitrophenine yellow (Collodion emulsion).

Deliver a strong band from CÂ ° /, D to above F, so appear very suitable for the purposes of three-color printing (images behind green filters). This dye is also suitable for drying plates if the aqueous solution of the same is used as a bath liquid without ammonia. With such bathing plates you get a completely closed band with longer exposure, which, starting behind D, extends to over%, which is very desirable for some purposes. (S. -Eig; 22).

Nitrophenin yellow, which belongs to the same group, has a similar effect on drying plates as thiazole yellow '). The same thing gives a completely closed band in half the time, which starts at D and

!) From the "The Clayton Aniline Comp.", Manchester.

Investigation of tar dyes on their ability to sensitize them to bromide silver. 141

before ended. In the case of Collodion plates, the tape begins behind D and extends to F. Both dyes \_ represent valuable green sensitizers.

These dyes are used in concentrated alcoholic solution for Collodion emulsions. The most suitable amount of these solutions as an additive to the Collodion emulsion is 10  $\frac{1}{100}$ , the concentration of the Silver bath 1: 500. For drying plates, 50 cm?  $\frac{1}{100}$  of the solution 1: 500 in water without ammonia, with 500 cm? Diluted water to use as bath fluid.

Diazo solid black 3B has a strong effect, gives dry plates a band from B to D with a maximum at B! /, C | |

Diazo fast black BHX sensitizes drying plates almost evenly up to a; in the case of a longer exposure, an indistinct maximum can be established at C ' /, D.

Pluto black CR only gives a weak band from 2 to C \* /, D with a longer exposure without a clear maximum. | |

Diamantschwarz FB, patented, is a very powerful sensitizer for dry plates, you get a sharply delimited band which extends from a to C  $\frac{1}{100}$  /, D, with the maximum BJ, C. This dye works on Collodion plates. much less favorable; you get a weak band between A and: E52: |

Dyes from Holliday & Sons in New York.

The Holliday & Sons company in New York provided us with a large number of dyes for experimental purposes through their representative in Vienna, Mr. G. Weiss, some of which proved to be very useful sensitizers. Almost all of the colors known as amidazole dyes showed more or less sensitizing effects, and with all but one, this effect consisted of an almost continuous lengthening of the spectrum towards the red end of the same, the effect only at a longer exposure results in printing. Amidazol-Green, -Grey B, - Gambir, -Cachou and four brands of Amidazolschwarz were examined, whereby the following results were obtained:

Amidazole Green B. The dye dissolves fairly easily in water; it is insoluble in alcohol. Adding ammonia to the aqueous solution does not change the color. The aqueous solution absorbs the yellow, green, and blue rays fairly evenly in the orange-red; at X - 612 wu there is a little noticeable band. In a bath which contains 2  $\frac{1}{100}$  /, dye solution (1: 500) and 2  $\frac{1}{100}$  /, ammonia, sensitized bromosilver gelatine dry plates show no sensitizing effect on short exposure. With long exposure, the effect of 5b begins and shows a very blurred, barely noticeable band at C ' /, D.

Amidazol-Gambier behaves in a similar way to the previous dye, only the almost continuous sensitization effect extends to B with long exposure and the appearance of an indistinct band from E3 /, D to C can be noted. The same is true of amidazole cachou, a brown dye that is insoluble in alcohol.

Amidazole gray B is not very effective; with shorter exposure it doesn't work at all;  $\frac{1}{100}$  When the exposure is very long, an almost continuous sensitization effect can be seen, the same closes at  $\frac{1}{100}$  with the suggestion of a narrow band. |

Amidazole black. Four brands of this dye were examined, namely amidazole black G, 2G, 4G and 6 @. |

These dyes all dissolve fairly easily in water; they are sparingly soluble in alcohol. With the exception of the 6G brand, they only give a sensitizing effect after long exposures, and although the same is usually a continuous one (with the 2G brand almost reaching to A), only the Amida-

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zorgelb 6G makes an exception in this regard in that it shows a clear band with the maximum D?

/, E even with a short exposure).

Another interesting group of dyes of the mentioned color works are the "titanium colors" (which, however, have nothing to do with the metal "titanium"). The following were examined: titanium scarlet (brands B, D, G and SS), titanium yellow and titanium black. Brands B and D of the four samples of titanium scarlet showed very similar behavior. They are all more or less easily soluble in water, as well as in alcohol. The more or less yellowish, red solutions in water do not change their color when ammonia is added and absorb the light in the yellow-green and green almost evenly; where tapes appear, they are washed out. As far as the sensitization capacity of these dyes is concerned, the brand B shows an extremely low sensitization capacity for silver bromide gelatine plates, which is manifested in a lengthening of the spectrum towards the less breakable end with long exposure. At brand D an indistinct band at D against E can be seen. Brand G shows a much clearer band, extending from C to D  $\frac{1}{2}$ , E, with the maximum at D $\frac{2}{2}$ .

The behavior of the "Titan Scarlet S" is completely different from these dyes. This dye dissolves easily in water and alcohol with a scarlet color; the aqueous solution stains bromide-silver quite easily without an excess of silver, and in a somewhat more concentrated solution it completely absorbs the rays of C!  $\frac{1}{2}$ ), and towards the more frangible part of the spectrum, so that corresponding end concentrated solutions of this dye would make very useful color filters for the purposes of three-color printing.

More dilute solutions show a maximum of the absorption in the green-blue (between E and F), while in the blue and violet (from F to over G) more light is let through.

However, the behavior of this dye against bromide silver emulsion plates is interesting. Titanium Scarlet S acts as a powerful sensitizer on both silver bromide gelatine and silver bromide collodion. Give bromosilver gelatin dry plates, bathed with the aqueous solution containing 2% ammonia (1 part of dye, 40,000 parts of water), then allowed to dry and exposed in the spectrograph, a spectrum which, with a short exposure, is almost identical to the bromosilver band shows a strong band extending from B  $\frac{1}{2}$ , C to D  $\frac{2}{2}$ , E, while longer exposure results in a closed band of almost the same thickness, extending from B to A (see Fig. 23). Significantly more powerful effects can be achieved if the bath liquid is used to sensitize to 100 cm? Add 1 to 2 drops of silver nitrate solution 1:40, but the plates will not last that long and must be dried and used up within two days. If this dye is just as suitable, it can be used directly for staining bromosilver gelatine. should be called to play a role in the production of so-called "pan- chromatic plates" in practice.

The dye also works with bromosilver collodion emulsions when it is 10 cm? on 100cm? Emulsion of the latter is added as a very powerful sensitizer. Even with short exposures, the broad band of sensitization, which extends from: a to over E, is clearly visible. The maximum of the sensitization is at C  $\frac{1}{2}$ , D.



The effect of titanium scarlet S on silver bromide emulsified in gelatine and in collodion is shown in Fig. 23 on p. 143.

1) These amidazole black dyes, which have a very similar effect, are the dyes Katigen black 2 B and Katigen blue black 4 B, which Ms. Bayer in Elberfeld has brought to the market, which also become almost continuous up to a, respectively above, with longer exposures there were spectra reaching out.

?) The whale scarlet fever marketed by the same company is very similar to this dye as a sensitizer. The aqueous solution of the same tolerates ammonia, stains bromide-silver only a little and gives, when used as a sensitizer in bromide-silver gelatine drying plates, already with a fairly short exposure besides the continuous lengthening of the spectrum in the less frangible part a clear, if not a very strong bond from G5Debis DIE.

Investigation of tar dyes on their ability to sensitize them to bromide silver. 143

Titanium yellow comes on the market as a brown-yellow powder, which easily dissolves in water with a reddish-yellow color, as well as in alcohol (golden-yellow). The solution is modified by ammonia and colors bromide silver without excess silver nitrate. The aqueous solution, when concentrated, absorbs all light from E on towards the more breakable end of the spectrum; More dilute solutions of the dye show an absorption advancing from F towards F', G.

The aqueous solution 1: 5000 gives bromosilver plates a sensitivity ranging from D to almost 7, with the maximum between F and G (corresponding to that of pure bromosilver gelatine plates).

However, this effect only occurs when the exposure is a little longer; the received tape but is then a completely uniform from D to A! /, H, Z

. | The, 28;

AabC:;, D :. Bbi, FR H h H

1. Bromosilver gelatine plate, sensitized with an aqueous solution of titanium scarlet S containing ammonia without added silver nitrate. 2. Bromosilver gelatine plate, sensitized like 1, but with the addition of silver nitrate solution. 3. Bromosilver collodion emulsion bathing plate. Titanium black. The aqueous, violet-red solution of this dye absorbs the light from red to violet and shows a maximum at the border of the Å – orange-red. The sensitizing effect is expressed in a rather strong band from D \* /, C to B' /, a with the maximum at C' /, B. The dye gives bromide silver a faint, dirty purple-red color.

Ingrain Black B dissolves fairly easily in water, but not in cold and hot alcohol. The aqueous solution is not changed by ammonia and stains bromide silver only slightly and slowly. With a slightly higher concentration, it absorbs the yellow, green and blue rays. When used as a sensitizer, you get a strong color with the dye at medium exposure

Sensitization band, ranging from B to D, with the maximum at C! /, D. 144 | E. Valenta.

Acid black gave just as little useful results as "Alizarin black 22,279", in that Sensibi only gave long exposures ization occurred in the less frangible part of the spectrum, and only to such a lesser extent that these dyes appear to be practically irrelevant.

Of the other dyes examined, the following should be discussed at this point:

Disulfine blue is a dye which is soluble in water and cold alcohol and has an intense blue color, which does not change when ammonia is added. The aqueous solution stains bromide-silver poorly and absorbs orange-red, yellow and green. The maximum of the absorption band is at

A600 uu. The dye is a weak sensitizer; a faint band from DY, C to C is obtained only after longer exposure.

Genuine chrome blue is a dye that is light in water and somewhat heavier in alcohol, with a violet color, and its solutions are discolored by ammonia. The aqueous solution gives bromosilver a weak color and absorbs yellow-green and green.

Genuine chrome black behaves similarly to the previous dyes. The dye is heavy in alcohol and easily soluble in water with a red-violet color. The latter solution shows an indistinct absorption band with the maximum at 620 uu. The dye turns silver bromide a moderately dirty red.

Plates sensitized with the aqueous solution containing ammonia give a band from D! /, C to a, maximum at B! = 650 un) with medium exposure.

Real chrome green, a dye that is easily soluble in water with an emerald green color, and also in alcohol with a blue-green color. The aqueous solution is not changed by ammonia and gives a broad absorption band, which in the case of concentrated solutions decreases slowly from D to E and increases to the more breakable end at F! /, G. More dilute solutions give three bands, the maxima of which lie at (, C ° /, D and in the violet part of the spectrum.

Drying plates sensitized with the aqueous solution of the dye in water (125,000) containing 2% ammonia show a sensitivity in the red part of the spectrum. At medium exposures, there is already a fairly strong band, reaching from A to C, its maximum at Beast, received.

Dyes from other factories.

A number of older dyes were specially tested for their ability to sensitize them to Collodion emulsions. Among these, various acid violet from the Baden aniline and soda factories produced a weak sensitizing effect, the maximum of which is D. Naphthyl blue (Kalle), band from B to D with the maximum C! /, D had a strong effect. Various nigrosines gave unfavorable results; weak, narrow bands in red and Å – orange red were only obtained after a longer exposure time. Very weak bands also resulted in muscarin green (Durand, Huguenin & Co.) and Nyanzaschwarz (Baden aniline and soda factories).

A number of black dyes have finally been tested for their dry plate sensitivities. This resulted in: Kohlschwarz II (Meister, Lucius and BrÃ¼ning) with a longer exposure a sharply delimited, very narrow band immediately adjacent to D.

Naphthylamine black 4 B (Cassella), with longer exposure a weak band from a to C! /, D and a second similar band from D! /, E to DÂ® /, E. | | Diamond deep black SS (Cassella). With a short exposure, a fairly strong band appears, extending from a to C? /, D; with a longer exposure, a second one, extending from C / to CÂ® /, D begins to become visible. The brand A of the same dye gives a strong band from a to CÂ® /, D with a short exposure, and a second band from D \ J

/, E to D? /, E, maximum D '! /, E with a longer exposure , while the SOO brand only covers the former tape. from a to CÂ® /, D there,

Investigation of tar dyes on their ability to sensitize them to bromide silver. 145 Wollschwarz 6B (Actiengesellschaft für Anilinfabrikation) works just as well as the brand 45,

which I recommended a year ago as a sensitizer!) And which since then has been used as a red sensitizer for the purposes of three-color printing on the k. k. Graphic teaching and research institute is in use. On the other hand, the GRD brand looks much less favorable. You get a narrower band, going from B to C! /, D. | | |

Nerol (Actiengesellschaft für Anilinfabrikation) has an unfavorable effect and only gives a narrowband at B <sup>1</sup>/<sub>2</sub>, C with long exposure.

Finally, a black dye from Cassella should be mentioned, which was produced according to D.R.P. No. 105.200. It gave a fairly strong band of sensitization, going from a to C <sup>1</sup>/<sub>2</sub>, D, the maximum of which is at C.

1) "Photographische Correspondenz", 1900, February issue, p. 99 ff .; these treatises, p. 138. 19th

Investigation of tar dyes on their ability to sensitize them to bromosilver gelatine rock plates in the visible part of the spectrum.

Of

E. Valenta.

("Photographische Correspondenz", 1902, p. 209 and 262).

The following Studies published at the end of the year cover more than 140 different, partly newer, dyes, which the factories in question made available to us on request. These include dyes which appear to be particularly suitable for playing an outstanding role in the manufacture of "orthochromatic" or "panchromatic" plates.

rapie testing of the dyes was carried out in the manner already described in my earlier papers on the subject. The individual dyes are discussed in groups comprising the products of the respective factories.

Dyes from the paint factories formerly Fr. Bayer & Co. in Elberfeld.

Anthracene red (!), Brown-red powder that is soluble in alcohol and water, is not changed by ammonia and colors neutral bromide-silver moderately. With longer exposure, this dye gives two bands of sensitization, a wider, faded band at D and a sharp, line-like band at a. The bromide-silver maximum suffers an apparent shift towards F.

Azo-Eosin?), Orange powder, soluble in alcohol and water with a red color. The solution does not stain neutral bromide silver. Weak sensitizer. With longer exposure almost continuous effect up to a.

Brillant-Geratin B. Composition not published. Like brand 3 B, it dissolves in both alcohol and water. Weak sensitizer. Increases the sensitivity in the blue when the bromide silver maximum is shifted to F. In the green in Roth, sensitization occurs continuously with very long exposure. The same goes for grade 3B.

1) benzidine dye. 2) Orthoanisidine - "-Naphtholsulfonic acid

NW. Investigation of tar dyes etc. | 147

Geratin BB and G. Den Ericas-like dyes (€), have a very strong effect in the blue, without changing the position of the bromide silver maximum and without impairing the clarity of the negatives. |

The dyes are soluble in alcohol and water. The solutions are not changed by ammonia and hardly color neutral bromide silver. Brand BB gives a band from C to D.

Congo Orange G and R ?. Of these two dyes, only the latter is effective. It is a red-orange powder, soluble in water; the solution is not changed by ammonia and does not color neutral bromide silver.

Sensitized from C <sup>1</sup>/<sub>2</sub>, D to D <sup>1</sup>/<sub>2</sub>, E, maximum at D <sup>1</sup>/<sub>2</sub>, E. Blue effect strong predominantly. Mikado-Orange G. Orange powder, easily soluble in water, hardly soluble in alcohol, hardly stains bromosilver. Does not sensitize in green, but yellow increases the coverage in blue.

Brilliant yellow does not work, encourages fogging.

Chloramine yellow G and M. Brown to brownish yellow powder, soluble in water and alcohol. Ammonia does not change the solutions. Bromide silver is not colored much. These dyes  $\hat{\text{A}}^\circ$ ) \_ Sensitize, just like the chloramine orange, in green-blue and blue. There is an (apparent) shift of the bromide silver maximum towards F; the effect extends to over 2 with longer exposure.

| Chrome yellow D and R. Both dyes show a very low sensitizing power. The blue effect is intensified with Chrome Yellow D. Diamond flavin G does not work.

Diamond yellow G, a dye \*), which, like the diamond yellow R, only contains bromide silver weakly colored, sensitized with short exposure in blue-green, so that the sensitization maximum comes to rest at F. With a long exposure, a band extending from C', D to  $\hat{\text{C}}^\circ$  /, D is obtained. Kresotin yellow  $\hat{\text{G}}^\circ$ ) and  $\hat{\text{R}}^\circ$ ) do not stain bromine silver in an aqueous solution and both sensitize them in blue-green and blue. The maximum of the silver bromide effect appears shifted to # and the sensitizing effect in the case of the cresotin yellow G extends over 5b towards the less breakable end of the spectrum. Even in high concentrations, the dyes only color the gelatine a little and the dye is easy to wash out.

Mikado yellow looks similar to mikado orange. The bromosilver maximum is shifted to F. Diamond green?), Soluble in water with a blue color. Ammonia changes the color of the solution to reddish-violet; it does little to stain bromide-silver.

This dye has a sensitizing effect both in the blue, where it intensifies the nature of the bromide silver, and (but only after longer exposure) in the red, where a band from a to C with the maximum at D occurred.

Alizarin-Sapirol B, green-black powder, not in alcohol, but soluble in water. The solution is not changed by ammonia, and silver bromide does not color it. The dye is strong

1) Probably obtained by coupling dehydrotoluidine or xylidine with 1: 8 dioxynaphthalene (4) sulfonic acid (Loewenthal: "Handbuch der Färberei", II. Vol., Pag. 914). Ss-naphthoedisulfonic acid R phenetol. 3) They are made from dehydrotoluidinsulfosa ure obtained by treatment with chlorinated lime or other oxidizing agents. # 4 C, H, (COOH) .N = N.C, H, OH.COOH; Loewenthal, a. a. Cit., Vol. II, p. 1084.

2) toluidine <

2 cresotinic acid) De es euineanre, 6) Tolidin Setorglinsähte cresotinic acid.  $\hat{\text{A}}^\circ$ ) Azo dye:  $\hat{\text{A}}^\circ$  OHGH; = COOH

> N = NC, H, N = NC., H, OH, SO, Na. 19 \*

re is 1 \_ SCHE EBIEBRENE, 2) he 222  $2\hat{\text{A}}^\circ$  A 1 VEERE REBRENEERSE 148 E. Valenta.

in blue, maximum at F. With longer exposure, two thicker stripes at a and at C can be seen in a continuous band that extends from A to E.

Celestine blue B gives heavily veiled negatives and depresses the plates' sensitivity to blue: Gallamine blue, which is related to it, behaves analogously to this dye}).

Dolphin blue 3?) Dye soluble in alcohol and water; the aqueous solution stains bromosilver quite strongly. Sensitized in the blue and blue-green part of the spectrum; the maximum is at  $\hat{\text{d}}^\circ$  /, F, the band is directly connected to the bromide silver effect. With long exposure continuous effect up to A, with indistinct bands reaching from C to D.

|

Diazurin BD. Dye of unknown constitution. Soluble in alcohol and water; the blue, watery solution is colored red by ammonia; it colors bromide silver and sensitizes strongly, both in

yellow to red (band from B to D! /, E, maximum C /, D), as well as in blue-green and blue (band starting from E, maximum at 5 ? /, F). |

Indon blue 2B and 2R. With normal concentration of the bath fluids, these coloring agents cause fogging. They give bromide a strong color. With brand 2R, at strong dilution (1: 200,000) without ammonia, clear plates are obtained which, when the blue sensitivity is depressed, result in a band ranging from B to D, with the maximum at C.

Intensive blue®). Dye easily soluble in alcohol. The aqueous solution stains bromide silver quite strongly and sensitizes dry plateaus strongly, both in the blue (shift of the maximum to F) and in the red (band from B to CÂ® /, D, maximum at D) .

Katigen indigo. Blue, water-soluble powder. The aqueous solution colors bromide silver strongly and sensitizes continuously and (with longer exposure) strongly from F to A, but makes the plates veiled in normal concentration.

Lazulin blue R. Soluble in alcohol. The aqueous solution gives bromide a strong color, causes fogging. Sensitized weakly from C to D, maximum C! /, D.

Rosazurin G \*) and B. Brown-red powder, soluble in water, not soluble in alcohol. The solution is almost unchanged by ammonia and strongly colors neutral bromide silver. In the case of medium exposures, a strong band, reaching from C to E, maximum at D. Blue effect predominates strongly.

Direct bronze brown?). Brown powder, insoluble in alcohol, slightly soluble in water. The aqueous solution does not stain bromide-silver. Sensitizes dry plates from B to D, maximum C DR at medium exposures, but increases the tendency of the plates to form fog.

Chloramine brown G. Similar to chloramine yellow, sensitizing in blue. The same applies to themikado brown.

Phenyl Blue Blackâ € N and Alizarin Cyanine Black do not sensitize; the latter dye strongly reduces the sensitivity of the plates in the blue.

Paint factories Leopold Cassella & Co. in Frankfurt a. M.

Croccein 4.2. does not have a sensitizing effect. Lanafuchsin SB acts as a weak sensitizer in the purple areas of the spectrum. Toluylenroth acts as a weak sensitizer with longer exposure continuously up to above C.

!) Both are gallamic acid derivatives.

2) derivative of gallocyanin.

3) Constitution not published. Acid dye.

Aethyl B-naphthylamine sulfonic acid F. ß-naphthylamine sulfonic acid F.

5) Direct cotton dye, constitution not published. SeRolidin with

Investigation of tar dyes, etc. 149

â € šImedial Blue C does not dissolve in alcohol, the dye is soluble in water, the solution stains bromine silver slightly and does not sensitize dry plates very much in short exposures; with longer exposure and especially with strong initial effects, negatives from A to H were almost completely evenly covered. Unfortunately, this dye gives the plates a certain tendency to fog and stain.

Imedial brown gives a weak continuous lengthening of the spectrum image to A.

Thiocarmin R gives a narrow, sharp band from a to 5 with the maximum AY, B)) when the blue sensitivity is depressed. |

Anthracite black B does not have a sensitizing effect.

Half-wool black is not soluble in alcohol, easily soluble in water, and bromide-silver does not color. The aqueous solution sensitizes dry plates weakly in orange, yellow and red, band from Dbis (, maximum D1 /, C.

Imedial brown B, a dye that dissolves easily in water, strongly colors bromide silver and, in a somewhat stronger concentration, is used with the addition of ammonia ned, sensitized vigorously and evenly from A to over E with longer exposure. The bromosilver maximum suffers an apparent shift towards F, where the strongest effect is recorded in the entire spectrum. The effect of the imedial black V is analogous and differs from that of the imedial brown only insofar as there is no shift in the bromide-silver maximum. '

The best concentration is for Imedial Black V 1: 5000, for Imedial Brown 5 1: 15,000 and 1Å ° /, ammonia.

Dyes from the Baden aniline and soda factories in Ludwigshafen a. Rh.

The red dyes Orseilleroth A, Palatinroth A, Palatinescharlach A, 3R, AR, Rosaflavin and Salmrothproved to be as good as without sensitizing effects.

Thiazinroth GundR, two dyes which are both easily soluble in water and whose constitution has not been published, behave quite differently as sensitizers. While the brand G only has a sensitizing effect after longer exposure and provides a weak band with the maximum C! /, D, the brand R is a very powerful sensitizer for the area from B to E and the maximum C \* /, D. With longer exposure the effect is panchromatic.

Pyraminorange G and R have a sensitizing effect in blue, which in turn increases the effect of the silver bromide. The same applies to cotton yellow 5G and wool yellow.

Blue-green S strengthens the silver bromide effect.

KryogenblauG is a dye that is not very soluble in water. The concentrated aqueous solution, diluted four times with water, was used to sensitize the plates after adding 2% ammonia. You get two faint bands, one from B to C, the other from OD to D \* /, E, with the maximum at B ' /, C and D.

Night blue?) Gives the gelatine a strong color and reduces the blue effect with strong coverage.

||

Oxamine blue B acts as a weak sensitizer, band from B to D, with an indistinct maximum. Cryogenic brown, easily soluble in water, which only weakly colors bromide silver.

The aqueous solution has a strong sensitizing effect in the blue (shifting the maximum against the

1) In this respect, this dye is similar to certain types of Capri blue, which give a very sharp, narrow band at A without otherwise having a sensitizing effect. 2)

Tetramethyltolyltriamidodiphenyl naphthylcarbinol hydrochloric anhydride.

A m or n n g ve ae r ir Pr.

W150 E. Valenta.

less breakable end up to just before F) and with longer exposure strong at C, unfortunately also disruptive to the formation of fog. |

Oxamine marron dissolves in alcohol and water. The aqueous solution stains bromide-silver moderately. Sensitized from B to D ' /, E (indistinct maximum). |

Cotton Black D, an azo dye, the constitution of which has not been published. Soluble â € œ in alcohol and water. The aqueous solution stains bromide silver strongly. In an ammonia-

containing solution, the dye acts as a powerful sensitizer even when very diluted. Well covered band from A to over D, with the clear maximum at BY, C

Anthraquinone black is a sulfur dye of unknown constitution. Does not dissolve in alcohol, but easily in water and works continuously up to B, the coverage, with longer exposure

is a strong one here.

Farbwerke formerly Meister, Lucius and Br  ning in H  chst a.M.

Alizarin granat R is a red color soluble in water containing ammonia, which stains bromide silver only slightly and has a weak sensitizing effect in the less breakable part of the spectrum (with long exposure a weak band from C to D! /, E becomes the maximum D!, E obtained) acts. A similar effect was obtained with garnet in dough form 2097, ig and azarin S; the latter dye gives a weak band between D and E (maximum DJ, E) on long exposure.

Alizarin yellow GG @ W and N only resulted in an increase in the Eapindichleit in blue, without the intrinsic effect of the bromide silver being impaired.

Naphthalin green TV ("), slightly soluble in alcohol and water, stains bromide-silver very little. Longer exposure gave two. Very narrow. Clear bands at A and between B and C (maximum B14

/, C) received. |

Ethyl blue BF does not sensitize, but rather strongly reduces the general sensitivity of the bromide silver even in a very dilution (1: 200,000). It is interesting to note that this dye gives bromide a strong color (it is likely to change in the process). |

Highest new blue. O  , the dye related to water blue, is discolored by ammonia, stains bromine silver little and gives - with longer exposure - a strong band from C! /, D to B? /, D with the maximum C1 /, D

Thionine blue GO). Dye soluble in alcohol and water. Related to methylene blue, silver bromide has a strong color, but has a strong haze-forming effect even with a very low concentration of the dye. Risk art. Awareness tape from B to C (maximum BY, C).

Dianil black N. The dye does not dissolve in alcohol, easily in water. Ammonia doesn't like the narrow and gives bromide silver a strong color. Even with very short exposures, the dye gives a strong band from B to before E (maximum C   /, D). With a longer exposure, a second, fairly strong band appears at A. With a correspondingly long exposure, a closed band is obtained, ranging from infrared (Z) to ultraviolet. This dye is one of the most powerful among the previously known red sensitizers and in its effect the wool black

4B  ) very similar.

1) Dye whose constitution has not been published. 2) Chlorzinc double salt of trimethylethylthionine chloride. (Loewenthal, op. Cit., Pag. 732.)   ) From the stock corporation for aniline production in Berlin.

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Chemical factory formerly Santoz in Basel.

Trisulfonviolet B, violet dye, not in alcohol, easily soluble in water; colors bromosilver only weakly and only gives a band from A    to D with longer exposure with an indistinct maximum at: CH, D. |

Direct Indon blue R!). Blue-black powder, not in alcohol, easily soluble in water. The solution turns violet on the addition of ammonia, but bromide-silver turns a little color. The dye strongly sensitizes from B to D (maximum at ()).

Melogen blue BA!) Behaves very similarly to the previous dye, only the maximum is slightly shifted towards the more breakable end; it is at C  $\frac{1}{2}$ , D.

Trisulfone blue B!) And R!) Does not dissolve in alcohol, easily in water; the solution hardly stains bromide silver. The two dyes are weak sensitizers and only work after long exposures. Brand B gives a band from B to C  $\frac{1}{2}$ , D (maximum at D  $\frac{1}{2}$ , C), brand R a band from B  $\frac{1}{2}$ , C to C  $\frac{1}{2}$ , D (maximum at C). Both significantly increase the effect in the blue and give clear panels. Brune pure does not sensitize and depresses the general sensitivity of the plates.

Trisulfone brown B!) And G!). Brand B works continuously with longer exposure up to 5 and has the property of trisulfone blue to increase the coverage in blue. Brand G also gives a clear band from C to CY  $\frac{1}{2}$ , D (maximum C  $\frac{1}{2}$ , D) with longer exposure.

Direct-Schwarz TV!) Behaves very similarly to Trisulfonbraun R; with longer exposure faded band from C to over D with indistinct maximum at C  $\frac{1}{2}$ , D).

Farbwerk M $\frac{1}{4}$ hlheim, formerly Leonhard & Co. in M $\frac{1}{4}$ hlheim i.E.

Mikado-Orange GO and 3 RO?) Does not sensitize in the less frangible part of the spectrum, gives the plates a tendency to form fog with intensification of the blackening in blue and violet. Orange TA?) Dissolves in water with a red-brown color, also soluble in alcohol. Does not stain bromosilver. Powerful sensitizer; even with a short exposure a strong band with the maximum at D  $\frac{1}{2}$ , E occurs, which with longer exposure reaches from C to and adjoins the band in the blue, so that a closed band from C to H results.

Brilliant yellow?  $\hat{A}^{\circ}$ ) hardly stains bromide silver, sensitizes weakly continuously, extends the spectrum image; Above F, so should sensitize in the ultraviolet.

Mikado Yellow G and Mikado Gold Yellow 8G behave in a similar way. The latter dye also increases the blue effect considerably, which is also the case with Solidgelb.G.

Eboli green F!), A green dye that is easily soluble in water, gives bromide a strong color. Good sensitizer, works even with short exposure. Band from a to D  $\frac{1}{2}$ , E (maximum at B  $\frac{1}{2}$ , C). There are clear negatives.

Cressyl blue 2 BS, the dye related to Capri blue. Easily soluble in alcohol and water. The blue solution is colored red by ammonia and gives bromide a strong color. Narrow band from a  $\frac{1}{2}$ , B to B  $\frac{1}{2}$ , C (maximum at B). The plates don't give completely pure negatives.

Eboli blue R does not color bromine silver very little, looks continuous, but only after a longer exposure of

B to Eb, following on from the intrinsic spectrum of the bromide silver.

t) Constitution not published. 2) Like the various types of mikado yellow, it is prepared by boiling paranitrotoluenesulfonic acid with alkalis in the presence of various oxidizable substances. (Loewenthal, *ibid.*, P. 893.) Phenol.

3) Diamidostilbene disulfonic acid <| Phenol,

| 152 E-Vartenta:

Toledo blue V  $\frac{1}{2}$ ), water-soluble dye, does not stain bromide-silver, makes veiled negatives. Be. longer exposure shows a very narrow band at B with subsequent weak continuous sensitization. The blue effect is increased.

Akmebraund)), azo dye, soluble in alcohol and water, does not stain bromide-silver.

There are some vague negatives. With a short exposure a narrow band appears at C  $\frac{1}{2}$ , D, with a longer exposure a second one with the maximum B  $\frac{1}{2}$ , C is added and with a very long exposure a dr



ittes (maximum DFB). All three bands are narrow and the first very sharp, while the third is indistinct.

Mikado brown 2B and M sensitize weakly continuously. In the case of brand 2B, the lengthening of the silver bromide effect a narrow band at B! /, C.

Pegubraun G%), soluble in water, hardly stains bromide silver. Weak sensitizer. With longer exposure, band from B to over D (maximum at Ct /, D indistinct). Gives cause for the formation of a veil; increases the intrinsic effect of the bromide silver considerably.

Walkbraun 2!) And G)), dyes soluble in water and alcohol. The yellow-brown solution only slightly stains bromide silver and does not change the color when ammonia is added. Both dyes increase the blue effect. Brand B has a continuously weak sensitizing effect up to C after long exposure; Brand G shows a fairly sharp, very narrow band at BED:

Domingo chrome black M '). Water-soluble dye .. The dark purple solution turns blue when ammonia is added and colors bromide-silver quite well. Moderate sensitizer, with longer exposure a band from a to C! /, D (maximum at 3 ' /, C) appears; the blue effect of the bromide silver

is strengthened and the cover is stronger.

J. R. Geigy paint factories in Basel.

Chicago orange?), Brown powder with a brownish orange color, soluble in alcohol and water, stains bromide silver quite easily. Faintly sensitized in the less frangible part of the spectrum; only after longer exposure is an indistinct band from B to C ° /, D obtained. The dye, on the other hand, increases the blue effect of the panels.

Diphenyl orange!) Has the same effect as arnicaÂ °), which is related to the Chicago orange, and which gives the latter a rather strong color; sensitizing only in the blue area of the spectrum.

Diphenyl green!), Almost black powder, soluble in water with a yellow-green color. The solution stains bromide-silver pretty well. Absorbs the light in red and purple. Sensitized fairly strongly after long exposure; Band from B to C (maximum B1 /, C); strong reinforcement of the blue- violet cover.

Diphenyl blue®), a dye that is soluble in alcohol and water, colors bromide silver. Even with a short exposure, apart from an intensification of the intrinsic effect of the bromide silver, a broadband appears, from C to F, with the maximum at D. |

Diphenylindigo blue, blue-black powder, soluble in alcohol and water with a red-blue color; Bromsilver colors strongly and sensitizes strongly in blue-violet as well as in red and yellow. Strong band from B to CÂ® /, D (maximum at C) and (only with longer exposure) a strong band with the maximum DW, E.

1) Constitution not published. 2) Câ € "C, H, (SO, Na) NO I

Câ € "C, H, (SO, NaJ) N = NC, H, .C, H, NH ,. Â € œCâ € "C, H, (SO, Na) NO | I.

C-C, H, (SO, Na) N = NC, H, .OH (Loewenthal, op. Cit., P. 905).

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Diphenyl violet!), Soluble in water and alcohol with a fuchsin red color, stains bromide silver little, sensitizes well. Effect in blue and red. Band from C! /, D to C \* /, D (maximum C ' /, D), with longer exposure a second, weaker band occurs at D! /, E.

Diphenyl brown!) Only has a strengthening effect in blue and violet.

KerraCotbtasr) soluble in alcohol and water, colors bromide silver, works in blue and violet. In the less breakable part this dye gives an indistinct band at E to -DU /, E only after long exposure.

Diphenylblauschwarz '1) is a black-violet powder, insoluble in alcohol, but easily soluble in water with a dark-violet color. The solution has a weak coloration of bromide silver and has a strong sensitizing effect, both in blue-violet and in red. Even with a short exposure you get a fairly strong band, from B '1, C to CÂ° Â® /, D (maximum at C' /, D). Diphenyl black)) is an almost black powder, which dissolves in water with a purple-black color. It stains bromide silver. The solution 1: 3000 with 2Â° /, ammonia gives dry plates a good orthochromatic effect. Strong band, with medium exposures already reaching from A to over D (maximum at C). Strong coverage in blue and purple.

Eclips black !?) is a sulfur dye; it forms black pitch-like pieces that smell of hydrogen sulfide. The blue-black ammoniacal solution sensitizes with strong dilution (because of the tendency to fog formation on the plates treated with it) to above A into the infrared. The sensitization band begins before A and extends to BYJ, C (maximum A'j /, a). The plates show a tendency towards the red veil.

Isodiphenyl black R has a similar effect to diphenyl black R. It dissolves in water with a purple- black color, tolerates the addition of ammonia. The solution stains bromide-silver quite strongly and sensitizes strongly. Even with short exposures you get a band, from a to Â¼ Reaching above D, with the maximum at C. In addition, the effect is intensified in the area of the silver bromide sphere of activity. The plates work very clearly. The BolvpkenylschwarzD behaves in exactly the same way.

Actiengesellschaft für Anilinfabrikation, Berlin.

Columbia real scarlet 4B). Weak sensitizer. The red solution does not stain bromide-silver. Only after longer exposure do you get an indistinct band from C! /, D to DÂ® /, E (maximum at D). The gelatin layer is colored quite strongly red.

Erica 2B hardly sensitizes. Likewise Salmroth.

Columbia green?). Violet-black powder, dissolves in water with a dark green color, stains bromide-silver strongly and is a powerful sensitizer, which gives a strong band with a maximum of 3 even in very dilute solutions and with short exposure. Longer exposure results in a band from A to over D and increased coverage in blue and violet. Only very dilute solutions may be used, otherwise the panels tend to form a fog.

Columbia blue G, which only stains bromide silver slightly, is also a fairly powerful sensitizer, which gives a band from B to Â° /, D (maximum at C) at medium exposure.

Erie blue B, gray-blue powder, soluble in water with a blue color, does not stain bromide-silver. It only works with longer exposure. Band ranging from a to over C, with no pronounced maximum.

1) Dye, the composition of which has not been published. 2) primulin

- phenylenediamine. Naphtionic acid er 3) Benzidine dye (Nietzky: "Chemistry of organic dyes", p. 79).

20th

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Columbiabraun R, brown powder soluble in water. The solution does not stain bromide-silver. Sensitizes only after long exposure. Band from B to CÂ® /, D, then weaker effect, which follows on from the bromide silver effect.

Chromanil brown 2G, black powder, dissolves in water with a brown color, also in alcohol, and colors bromide silver. The aqueous solution sensitizes dry plates quite strongly. Band ranging from D to D<sup>+</sup>, E (maximum C<sup>+</sup>, D).

Sambesi brown 2G, gray-violet powder, soluble in water with a brown color. Acts as a powerful sensitizer for red and yellow; with longer exposure there is a strong band from A to D<sup>+</sup>, E (maximum at 6, D):

Attachment.

An interesting dye insofar as it sensitizes the blue-green very strongly, is the Auracin G of the Farbwerke formerly Fr. Bayer & Comp. in Elberfeld.

This dye has a powerful effect even in very dilute solutions (1: 25000); at a concentration of 1: 8500 one gets a strong band from D<sup>+</sup>, E to over F with the maximum at 51), F.

The auracin allows eosin dyes to be used at the same time, which means that sensitive plates can be obtained in both yellow-green and blue-green.

That from the company formerly Meister, Lucius, Br<sup>1</sup>/<sub>4</sub>ning & Comp. Dianil green G brought onto the market raises awareness in the Roth. Band from a to the silver bromide effect, maximum B<sup>+</sup>, C. At

long exposure, a faint narrow band appears in the ultra-red.

I.

Effect of some yellow dyes as sensitizers for silver bromide gelatin in the visible part of the spectrum.

Of

E. Valenta.

("Photographic Correspondenz", 1902, p. 199.)

With regard to their behavior as optical sensitizers for the visible part of the spectrum in the case of bromide-silver gelatin dry plates, the yellow dyes, which have been investigated by me so far, can be divided into several groups.

The first of these includes all those who have practically no sensitization ability or only give a continuous band with longer exposure, which, following the sphere of activity of the bromide silver, increases towards the less breakable end of the spectrum without the power of that Zone to reach. This group includes most of the yellow colorants, for example polychromine, arnica (Geigy), acid yellow, Indian yellow, Afghan yellow, whale yellow (Holliday), Mikado yellow, azo yellow (M<sup>1</sup>/<sub>4</sub>hlheim), chloramine yellow, chrome yellow, biamantflavin (Bayer) and others.

A second group of yellow dyes gives, without weakening the actual effect of the bromosilver gelatin plate, a strongly protruding band with the maximum between F and D, so that the same closely follows the sphere of action of the bromosilver gelatin, whereby with a correspondingly long exposure time, a uniformly strong, strong band extending from D<sup>+</sup>, E to over 7 is obtained.

This subheading includes nitrophenin (Clayton), then the Thiazole selb (Bayer<sup>TM</sup>), titaniumyellow (Holliday?) And others.

The third group of yellow dyes, which act as green sensitizers, is the most interesting. It includes, among other things, the yellow acridine dyes and two very similar yellow tar colors From Holliday & Sons: "Cotton Yellow II" and "Canary Yellow".

Treatment with these dyes results in an (apparent) shift in the silver bromide maximum towards the less breakable end of the spectrum in the case of silver bromide gelatine plates. At Chrysaniline, a yellow acridine dye whose sensitizing effect has been known for a long time,

1) Diazoamido compound from diazotized paranitraniline and dehydrotoluidinsulfonic acid. "Handbook of Dyeing" by Xnecht, Rawson and LÃ¶wenthal, 1900, Volume I, p. 909.

2) Diazoamido compound from diazotized dehydrotoluidinsulfonic acid and dehydrothiotoluidinsulfonic acid. Similar dyes are clay yellow and turmerine, which also work in the same way.

20 \*

156 h eve

this shift, which was recorded by Lohse!) as early as 1884, is only very slight. The maximum of the lighting effect is still between F and G. This shift goes much further with the others

Fig. 24. CD Eb F G h HK |

Silver bromide

gelatin. Chrysaniline.

Canary yellow.

Acridine

yellow.

-

\ Cotton yellow

II.

Nmmmen

Cotton yellow II and silver nitrate.

Sensitizing effect of some yellow dyes on silver bromide gelatine.

Spectrum photography, taken with the little Steinheil's glass spectrograph under gas light. of the yellow dyes mentioned, most closely to that of J. M. Eder and the author

investigated in 1894 and recommended acridine yellow as a sensitizer for green blue. This color

l) "Photographic Archive", 1887, p. 221,

Effect of some yellow dyes as sensitizers for silver bromide gelatine etc. | 157

In a saturated alcoholic solution, the substance is diluted in equal parts with water, without the addition of ammonia, used for bathing the drying plates. The gelatin layer is colored quite strongly yellow in this process and one obtains, since the maximum effect of the bromide silver is suppressed by the shielding effect of the colored gelatin, an apparent shift of the maximum towards green (Fig. 24). The maximum of the sensitizing effect lies between d- and F and: the bromide-silver maximum comes into effect only with very long exposures.

Two dyes from the Holliday & Sons company, Canary Yellow and Cotton Yellow II, whose chemical constitution I am unfortunately not aware of, have a very similar effect, but have a much stronger sensitizing effect. Both dyes are fairly lightfast and the colored powder in the glass changes its color by fading in the areas hit by the light. Both color bromide silver, which was obtained by precipitation with an excess of bromine salt, intensely yellow, and 5 to 10 parts of the solution 1: 500 to 100 parts of water are sufficient to make drying plates strong for District D '/, To sensitize E down to the ultraviolet. The maximum of sensitization lies between 5 and F; with canary yellow the same is located closer to F and there is also a second sensitization band between C and

D, so that with a very long exposure almost a closed band, reaching from C to the ultraviolet, is obtained. The plates sensitized with these dyes, in contrast to plates

sensitized with acridine gel solution, have the pleasant property of completely releasing the yellow color during washing, so that negatives with an uncolored gelatin layer result.

The plates sensitized with these dyes do not show the minimum of sensitization in the blue-green which most optical sensitizers give, which is sometimes of value in spectral analysis and for the purposes of color printing.

The reason for the shift in the maximum sensitivity of the drying plates treated with dyes of this group is the use of fairly concentrated dye solutions as sensitizing baths, whereby both the layer and the bromide silver are colored intensely yellow and act as a light filter muffled in the blue. For example, if you add a little silver nitrate solution to the sensitizing bath when using cotton yellow, which of the dyes in this group has the strongest sensitizing effect, the intrinsic sensitivity of the bromide silver is increased, to such an extent that the bromide silver maximum is that of the sensitization almost surpassed.

In this way, plates are obtained (see FIG. 24) which have an almost uniform band from  $\epsilon$  to H; Unfortunately, however, the treatment with silver nitrate not only increases sensitivity, but also increases the tendency to form fog, so that for practical Zinecker the Dye would be better to use without the additive mentioned.

The ability to sensitize some cyanine group dyes on silver bromide gelatin. Of

E. Valenta.

("Photographic correspondence", 1903, p. 359.)

Cyanine (quinoline blue) is one of the oldest red sensitizers; it gives the drying plates, which are bathed in the solution of the dye, a sensitivity to the orange-red and yellow-green rays. Long exposure results in a strong band from B to violet with a minimum at E, F and two maxima, one weak at  $E\frac{1}{2}$ , D and a strong band at  $D1\frac{1}{2}$ , C). A major disadvantage of this dye is the relatively low sensitivity in the yellow-green with not at all too great an overall sensitivity; HW Vogel combined the cyanine with quinoline red, and this is how the azaline was created? strongly depressed.

In addition to quinoline blue, a number of quinoline dyes have become known that are of no importance for dyeing purposes, since they are extremely light-resistant. For example, split wood represented a red-violet dye, quinaldine-quinoline-cyanine-ethyl iodide, which Professor Miethe examined spectroscopically for its sensitizing ability and, after he had recognized its value as a sensitizer for drying plates, used it under the designation "ethyl red" Manufacture of panchromatic plates recommended. The latter also examined together with Dr. Grape some homologues of this body. These dyes give a powerful effect in  $\tilde{A}$  – ranger red, yellow and green, which is so connected to the bromide silver effect with only slightly longer exposures that the very weak minimum in blue-green in the Fraunhofer line F is hardly recognizable is.

Dr. King in highest a. M. (Farbwerke vorm. Meister, Lucius and Br $\frac{1}{4}$ ning) represented a larger number of new dyes of the cyanine group. I have these preparations, which Dr. King was so gracious, the k. k. To make available a graphic teaching and research institute, subjected to a spectrographic test, namely the following dyes were tested and both with regard to the absorption capacity and the sensitizing effect on dry plates

examined:

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) Eder: "Photography with bromosilver gelatine", 1902, pag. 182.) S. Eder: "Yearbook for Photography and Reproduction Technology", 1887, pag. 310; "Photographic correspondence", 1886, p. 335.

The ability to sensitize some cyanine group dyes on silver bromide gelatin. 159

- . Lepidine-m-toluquinoline cyanine ethyl iodide;
- . Lepidine-p-toluquinoline cyanine ethyl iodide;
- . p-toluchinaldine -p-toluchinoline cyanine methyl iodide; . p-toluchinaldine-p-toluchinoline cyanine ethyl iodide; . p-toluchinaldine quinoline cyanine methyl iodide;
- . p-Toluchinaldine - quinoline cyanine ethyl iodide;
- . Quinaldine p-toluquinoline cyanine methyl iodide;
- . Quinaldine p-chloroquinoline cyanine ethyl iodide; NOREH oO We WO 5 BE SE> Em
- . p-toluchinaldine-p-chloroquinoline cyanine ethyl iodide;
- =)
- . Quinaldine p-methoxyquinoline cyanine ethyl iodide;
- 11. p-Toluchinaldine methoxyquinoline cyanine ethyl iodide;
- 12. p-Toluchinaldine -p-Bromoquinoline cyanine ethyl iodide.

The investigation of the absorption spectra of these cyanine dyes was carried out by means of a Kruss spectral apparatus in the visible part and by means of a Rowland concave grating in the ultraviolet part. According to these investigations, the tested dyes can be divided into two groups, the first of which comprises the lepidine-containing and the second of the other dyes. The lepidine-containing dyes dissolve in alcohol with a blue color; If sufficiently diluted, the solutions show a strong absorption band from  $\lambda = 625$  to  $\lambda = 574$  with the maximum approximately at  $\lambda = 591$ , next to it a second weaker band, the maximum of which is at lepidine - a -Toluchinolin- cyanine ethyl iodide about  $\lambda = 558$  nm. and in the case of the lepidine-p- toluquinoline cyanine dyes,  $\lambda = 545$ . The other investigated cyanine dyes give violet solutions and all show  $\lambda \pm m$  less breakable parts (orange, yellow-green) two absorption bands, the maxima of which were found to be approximately at  $\lambda = 560$  to  $573$  and  $520$  to  $525$ .

The sensitization ability of the dyes in question was tested in such a way that the substances in question were dissolved 1: 1000 in alcohol (or alcohol + water). From this solution 4 cm<sup>2</sup> on 200 cm<sup>2</sup> Water and 2 cm<sup>2</sup> ammonia were given and the plates were bathed for 3 minutes, rinsed with water, left to dry and exposed ... The exposure was carried out in the small glass spectrograph from Steinheil under gas light in the manner I described earlier, and individual dyes, which appeared to be particularly useful, and examined in sunlight with an instrument of greater dispersion (grating spectrograph). The spectra shown in FIG. 25 have been selected from the examined dyes. To compare the effect is also the spectrum recorded on a drying plate sensitized with Miethe's Aethylroth (quinaldine quinoline cyanine ethyl iodide) and shown in the figure, as it was obtained with a relatively short exposure time (selected the same for all dyes). The results of the spectrographic test of the examined dyes are given below. |

1. Lepidine-m-toluquinoline cyanine ethyl iodide. With a very short exposure, a strong sensitization band is obtained from C! /, D to D? /, E with the maximum at C /, D. With a slightly longer exposure, the band widens; it then extends from B! \, C to E, and you can see a second weak maximum at D? /, E, while with long exposures a very strong band from a to b with the

(apparent) maximum at D is obtained, which does not immediately adjoin the bromide silver effect, but is separated from it by a clear minimum (b to F).

2. Lepidine-p-toluquinoline cyanine ethyl iodide is very similar to the above dye, only the sensitivity in the less breakable part is 3 to 4 times as great and the transmission

The sensitization tape reaches from D to over E even with a short exposure. 160 | E. Valenta.

3. p-Toluchinaldine-p-Toluquinoline cyanine methyl iodide. In the case of a short exposure, the minimum at F can almost no longer be established; the volume appears continuously from C to

G. Man

notices a maximum just before D, a very weak minimum at D! \ / , â € œE, and a secondig: 29, BU. .D- Eb FR G h

p-Toluchinaldine-p-Toluquinoline ethyl iodide. p-Toluchinaldine - quinoline methyl iodide.

Aethylroth.

p-Toluchinaldine -? - Bromo "quinoline cyanine ethyl iodide. Quinaldine p-toluquinoline cyanine ethyl iodide.

Lepidine-p-toluquinoline cyaninaethyl iodide. Lepidine-m-toluquinoline cyanine ethyl iodide.

Spectrum photographs on silver bromide gelatine plates sensitized with cyanine dyes, using the small Steinheil glass spectrograph. Gas light added.

the maximum at D! ° Å® / , E, almost immediately following the effect of the silver bromide. With longer exposure, the band extends from BD to over h. The plates tend to be foggy. 4, p- toluchinaldine-p-toluquinoline cyanine ethyl iodide. The dye sensitizes dry plates very strongly; even with a very short exposure it already gives a closed band in which there is a maximum at D, a very weak, indistinct, subsequent minimum at D ! / , E and

reveal another maximum in front of E. Then there is a weak minimum behind F, followed by the The ability to sensitize some cyanine group dyes on silver bromide gelatin. 161

the silver bromide effect follows. With a somewhat longer exposure, the minima disappear, and one can only distinguish a very strong band extending from D! / , C to over h with a maximum at

D. Given its great effectiveness and high yield, the dye can be used very well for the production of panchromatic plates. The effect of this dye with short exposure can be seen from the figure.

9. p-Toluchinaldine quinoline cyanine methyl iodide is very similar in its effect to the previous dye. With a short exposure (see Fig. 25) one already obtains a closed band from B \ / , C to towards h, in which the maximum before D, a subsequent indistinct minimum at D \ / , E and a further maximum at D? / , E can be seen. With longer exposure, the effect extends to B and above. |

6. p-Toluchinaldin-Chinolincyaninaethyljodid is very similar to the previous one with regard to sensitizing effect, but with this dye the blue effect is much more evident, and the maximum at F is still clearly recognizable at medium exposures, and the effect is also sufficient Orange-red less than the methyl compound.

7. Quinaldine-p-toluchinolincyanine methyl iodide has a very similar effect to p-toluchinaldine- quinoline-cyanine methyl iodide. With a very short exposure one already



obtains a closed band from  $B \setminus \{C\}$  to towards  $h$ , in which a maximum in front of  $D$ , a weak minimum at  $D'$ ,  $E$  and  $a$

maximum at D? /, E can be seen . Longer exposures give a band from B to H with a maximum at D.

8. Quinaldine-p-Toluchinolincyaninaethyljodid always shows a minimum at F (b! /, F to F! /, G), even with longer exposure, but sensitizes very strongly in orange, yellow and green from C1 /, D to bY, F, in which band two maxima (just before D and at DÂ ° /, E) occur (see Fig. 25). With a long exposure you get a closed band from C to AH, in which you can clearly see a maximum at D and a minimum at 7. The plates work clearly.

9. p-Toluchinaldin-p-chloroquinoline cyanine ethyl iodide is a very clear, powerful sensitizer, but, like the one previously described, leaves the minimum (with this dye a little before F), even with longer exposure, clearly stand out.

10. Quinaldine-p-methoxyquinoline cyanine ethyl iodide is more closely related to the dyes described under 4; with short exposure times it clearly shows the minimum at 7 and one notices in the less breakable part of the spectrum a band of sensitization, ranging from C'1 /, D to 5? /, F, with two maxima (at D and DÂ ® /, E) and a weak minimum (for DJ, E); with longer exposure, however, you get a closed band from B to over h, with the maximum at D and the minimum behind F.

11. p-Toluchinaldin-p-Methoxyquinoline cyanine ethyl iodide differs only very little from the previously discussed dye with regard to its sensitizing effect. The two maxima in the sensitization band (at D and E) with the minimum lying between the same (at D \, E) unite with long exposure to a band whose maximum seems to be at DJ, E and which extends from B to A, whereby the minimum between the sensitization and the bromide silver effect (at F) remains recognizable.

12. p-Toluchinaldine-p-bromoquinoline cyanine ethyl iodide (see FIG. 25, fourth spectrum) shows a similar spectral behavior as a sensitizer to the chloroquinoline cyanine dye described, but with the difference that the plates have broader minima than in which have chlorine derivatives, of which that between 5b and F is particularly prominent, but give stronger maxima in the less frangible part of the spectrum. The company "Farbwerke formerly Meister, Lucius & BrÃ¼ning in Hoechst am Main" brings a dye under the name "Ortho- chrome T" to the market, which belongs to the group of dyes just mentioned.

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162 E. Valenta, The Sensitivity of Some Cyanine Group Dyes on Silver Bromide Gelatin. The effect of the "Orthochrom 7" is similar to that of the Aethylroth; but it extends further into the Roth than is the case with Aethylroth, which latter dye is also used by several companies for the purpose of sensitizing drying plates, among others. by Perutz in Munich. Since the "Orthochrom 7" of the company "Farbwerke formerly Meister, Lucius & BrÃ¼ning in HÃ¶chst a.

M. "In addition, it is cheaper than Aethylroth!), It should give this latter dye a strong competition.

With regard to the use of the sensitizing baths for the cyanine dyes discussed here, it should be noted that the sensitizing bath can be used a few times, but this must not be done so long that the liquid appears only slightly colored; on the other hand, used baths should not be left standing too long, since if such baths are left standing for a long time, a faint reddish precipitate is deposited and they lose their effectiveness. It is best to use the baths as much as possible, that is, to use only as much as you need to sensitize the desired number of plates and to pour the baths away after use.

Finally, it should be noted at this point that the investigated cyanine dyes have a property that is also shared by so many other sensitizers, for example wool black, dianil black and others. own to a large extent?). If you sensitize a dry plate with the cyanine dyes in question, if you put the plate in the developer after exposure (I used pyrogallol-soda developer), the sensitivity for red and yellow is so strongly reduced (to approx  $Y/10$ , the normal) that one can, without having to fear the formation of a fog, the development can be controlled by temporarily looking at the plate in the darkroom in the red light.

1) The "Orthochrom" costs 10 marks, the Aethylroth 30 marks per 1 g of dye. 2) See my treatise: "The sensitivity of orthochromatic gelatine drying plates to red and yellow light during development", "Photographische Correspondenz", 1902, p. 214.

Absorption and sensitization of some yellow dyes in the extreme violet and ultraviolet. Of

E. Valenta.

("Photographic correspondence", 1903, p. 483.)

In connection with my work, published on p. 155 of these papers, on the "Effect of dyes themselves as sensitizers for silver bromide gelatin", I examined the dyes listed there and a number of other yellow dyes for their behavior against the extreme violet ones and against them ultraviolet rays of light. To carry out these investigations I made use of a Rowland concave grating, the mounting of which, etc., was described in detail by J. M. Eder and myself on p. 163, Part I, of these treatises. The light source used in these experiments was either sunlight, which was thrown directly onto the gap in the apparatus by means of a heliostat fitted with a silver mirror, or the like the light from a bottle spark between electrodes made of Eder's alloy (Zn, Cd, Pb), which was concentrated on the gap by means of a quartz capacitor. In this case, the power source used to operate the inductorium was a direct current of 220 volts. A "Wood's roll" served as the inductorium!) In connection with some large Leydener bottles and a Wehnelt interrupter. With a power consumption of 6 to 8 amperes, this arrangement produced a very bright, "crackling spark" which, in addition to the spark spectrum of the Eder lead-zinc-cadmium alloy used as electrodes, also made the air spectrum clearly stand out.

The flame arc of a direct current of 110 volts between iron electrodes of 20 or 15 mm in diameter is also very well suited for investigating the absorption of light in the ultraviolet part of the spectrum; Such a lamp gives an extraordinarily linear spectrum, which is rich in violet and ultraviolet rays. |

Using one or the other of the above-mentioned artificial light sources in the first order spectrum, the absorption ratios can be followed up to almost  $\lambda = 210 \text{ nm}$ , while when sunlight is used as the light source, the ultraviolet spectrum is only up to about  $\lambda = 300 \text{ nm}$  could be observed. |

Aqueous solutions of the dyes were used to determine the absorption capacity of the dyes in different concentrations (1: 1000 to 1: 60000) in a plane-parallel quartz tank 10 mm thick

) Cf. pag. 170, Part I, of these treatises,

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Layer brought in front of the gap in the apparatus and photographed one above the other with the same length of exposure time with the aid of the sliding cassette.

To investigate the sensitizing effect of the dyes, the plates were bathed for 2 minutes in solutions of the relevant dyes, the concentration of which was 1: 2000 to 1: 10000, with the exclusion of any light and allowed to dry.

The results of these investigations of the dyes already discussed with regard to their sensitizing effect on bromosilver gelatine plates in the visible part of the spectrum: titanium yellow, thiazole yellow and nitrophenine, as well as acridine yellow, cotton yellow, canary yellow and nitrosodimethylaniline, can be seen from the enclosed Table IV, on which both the absorption spectrum as well as the sensitization spectrum of the dyes mentioned, as obtained when sunlight is used as the light source, is shown. |

If we take a closer look at Table IV, we find that titanium yellow, like thiazole yellow and nitrophenine, gives a closed absorption band in somewhat more considerable concentration, which in titanium yellow extends over the blue and violet as well as over part of the ultraviolet, while for the other two dyes it is considerably shorter and cuts off earlier against the more breakable part of the spectrum. Thiazole yellow absorbs all light in a concentration of 1: 3000 from  $\lambda = 444$  to the ultraviolet. At greater dilution (1: 10000) it reveals an absorption band which reaches its maximum at  $X = 387$  uu, while from then on to  $\lambda = 368$  the permeability increases and only then at  $A = 330$  complete absorption occurs again. Nitrophenine in particular soon cuts off because, with a relatively low concentration of the dye solution, complete absorption takes place from  $A = 476$  onwards.

The sensitizing effect of these three dyes in the violet and ultraviolet can be described as a relatively low one. In addition to the bromide-silver maximum, titanium yellow reveals a second indistinct maximum, whereas with thiazole yellow only a prolongation of the bromine-silver effect with almost the same force into the ultraviolet can be noticed. |

A similarly low effect can be observed when using nitrophenin as a sensitizer, as can be seen from the figure.

The filtering action of the three dyes is very interesting and characteristic: acridine yellow, cotton yellow, and canary yellow in the violet and ultraviolet parts of the spectrum. These dyes have sharp, clearly protruding absorption bands in the blue-violet and ultraviolet spectral regions.

Acridine yellow gives a strong absorption band with the maximum at  $\lambda = 430$  uu, to which a translucent band with the maximum  $\% =$  approx. 350 uu is attached. followed by total absorption. |

Canary yellow has an absorption band, the maximum of which is  $A = 483$  uu, and a second,. Such a band only appears at greater dilution, with the maximum at  $A = 366$ . The maxima of the permeability are  $A =$  approximately 386 un and  $X = 328$  un.

In the case of cotton yellow, there are also two pronounced absorption maxima. However, compared to those of canary yellow, they appear somewhat compared to the b more calculable end of the spectrum shifted; they are at  $A =$  approx. 407 uu and at  $X = 343$  to 350, the maxima of the permeability, however, are at  $A = 370$  and  $X = 320$  uu. The latter dyes have a sensitizing effect on dry plates in the violet and ultraviolet parts of the spectrum.

With canary yellow one gets from the band in the green and blue part, separated by a minimum, a: | broad: band. to A = approx. 300 un.

While cotton yellow shows the minimum further towards the less breakable part of the spectrum, the sensitizing effect only extends up to  $X = 340$  uu and this progresses

Table Is,

Spectrum photographs taken by means of the small grating spectrograph in sunlight. Ultraviolet

I. Titanium yellow. â € "I. Akridine Yellow. â € "II. Thiazole yellow. â € "IV. Nitrophenin. â € "V.

Canary yellow. â € "VI. Cotton yellow. â € "VI. Nitro

a = absorption spectra of the aqueous dye solution at different exposure times; b - sensitizationspectra

odimethylaniline. â € "VIII. Uncolored silver bromide gelatine. on the silver-bromide gelatin plates stained with dye.

Absorption and sensitization of some yellow dyes etc. 165

Band (probably as a result of the shielding effect) from Fraunhofer line K ( $X = 393$ ) to  $\% = 340$  fairly evenly.

At the end of panel IV is the absorption and sensitization spectrum of nitrosodimethylaniline, which R. Wood has examined very carefully with regard to the behavior of his solutions in ultraviolet light. | |

At a certain concentration, solutions of nitrosodimethylaniline have the property of absorbing the blue and violet rays of the spectrum, while only allowing the ultraviolet light to pass through in a slightly weakened manner, which is also the property of other yellow dyes. R. Wood therefore recommends the dye as a radiation filter.

The commercial nitrosodimethylaniline is a greenish-black crystal powder, which easily dissolves in water and alcohol with an intense yellow color. Subsequent to the above investigations, the solution of the salt in water was examined for its absorption capacity by serving as a light filter in various concentrations 1: 7500 to 1: 40000 in a 1 cm thick layer using a quartz tank in the grating spectrograph. The permeability of the tub filled with water and that of the same tub filled with the solution of nitrosodimethylaniline (1: 7500) showed only slight differences with regard to the permeability for the rays from  $\lambda =$  approx. 386 to the extreme ultraviolet, but absorbed strongly from  $X = 496$  to  $X = 886$  un.

According to the author's experiments, the triamidoazobenzene  $C_6H_3(NH_2)_3 - N = N - C_6H_3(NH_2)_3$ , has a very similar effect to nitrosodimethylaniline with regard to absorption in ultraviolet. The preparation used for the investigation was obtained from the Badische Anilin- und Sodafabrik and was a brown powder, easily soluble in water with a brownish-yellow color.

A solution of this body in water (1: 10000) absorbs green, blue-green, blue and violet light in a 10 mm thick layer up to the Fraunhofer line  $\eta = 397$  vu), and releases from there up to  $A = 320$  u, and with longer exposure beyond that the ultraviolet light passes through.

If you bath dry plates with the solution 1: 10000 to 1: 25000, you get a strong sensitization band, reaching from D', E, b, f, F, and with a somewhat longer exposure a closed band from D to over h, in which neither the bromosilver maximum nor that of the triamidoazobenzene (at 22) BE) can be recognized any longer.

Another dye which absorbs in blue and violet while transmitting ultraviolet, and only in a very small area, is acid yellow (from Holliday). This dye leaves in a solution 1: 10000, in a 10 mm thick layer, green and blue up to X = 466mμ. through and absorbs from then on except for a strip in the ultraviolet. The maximum permeability in the ultraviolet for this dye for the above- mentioned ultraviolet region is X = approx. 330 mμ.

Most of the dyes discussed above differ little in their spectral behavior in the visible part of the spectrum, but differ in their absorption in the ultraviolet; This also applies, as I have already convinced myself through some preliminary tests, to some other dyes, which have very similar absorption ratios in the visible part. I therefore commemorate this company to continue searches and to a number of chemically very different ones with regard to theirs

To expand absorption ratios in the visible part besides the spectrum but very similar dyes.

Behavior of some color sensitizers against the solar spectrum in the grating spectrograph. Of

E. Valenta.

The effect of the color sensitizers described in the preceding articles has been sufficiently clarified in the text as well as through curves and illustrations. The behavior of various photographic layers in relation to the prismatic spectrum has already been made evident in Tables I to III (see pages 80 and 98).

In panel V I present the heliographic reproduction of the spectral effect of some characteristic color sensitizers. The spectrum photographs shown there were produced using the sunlight reflected by a heliostat with mirror and a grating spectrograph with Rowland's concave grating of short focal length, as described on page 161, Part I, of this book, namely the spectrum First order was chosen because the clarity would suffer if the dispersion was greater. Greenish or pale yellow glass served as a light filter to filter out the ultraviolet rays. The spectra of the Roth sensitizers were recorded using yellow filters or Roth filters (copper ruby glass).

At the top of the three groups on this table contains the spectra of drying plates sensitized with Orthochrom 7, ethyl violet + erythrosine and titanium scarlet S.

The first of the mentioned dyes belongs to a group of quinaldine-quinoline dyes (see pag. 158), which all have the same character and are characterized by the dyes ethyl red (from Miethe), orthochrom 7 and pinachrom!) (From King in HÄrtel's a. M.) are represented. They show three maxima, namely at D, E and behind F. Even with a relatively short exposure, the three bands combine to form a closed band, which in the case of Orthochrom 7 extends from CU to over h. These dyes can be used with advantage in the manufacture of so-called "panchromatic" bathing plates. |

Of the three named dyes, the pinachrome gives the furthest after the less the frangible end of the spectrum and the plates most sensitive to Roth).

D) S. Ä «Photographische Correspondenz», 1903, pag. 173, 241, 311, 366, 885, 479 and 1904.?) To sensitize dry plates they are for 2 minutes in the following solution with exclusion of all light

bathed: 200 cm? Water | 3 to 4 â € Ž Pinachrome (solution 1: 1000 in water or aqueous alcohol)

n2,2 ammonia then washed for 3 minutes in running water and left to dry.p2]

Behavior of some color sensitizers against the solar spectrum, etc. 167

They work completely free of haze if suitable drying plates, for example Schattera or Lumiereplates, are used for sensitization with these dyes.

The second figure on the plate shows that by combining ethyl violet (see pag. 151), a dye that has proven itself in practice as a red sensitizer for three-color printing for the production of blue printing plates, panchromatic bromosilver gelatin dry plates with erythrosine can, which, however, are unable to bridge the minimum at b with short exposures, as is the case with Orthochrom. | |

The next illustration shows the effect of the "Titan Scarlet S" (cf. pag. 142), a dye which has proven to be particularly effective in sensitizing grainless emulsions for the "Lippmann Process". The following five figures (group II) show the effect of some green and black dyes, which I have tested and recommended as powerful red sensitizers (see above). Of these dyes, wool black 4 B from the Actiengesellschaft für Anilinfabrikation in Berlin was used to produce the negative for the blue printing plate in three-color printing (see p. 138).

The effect of this latter dye, as well as that of the columbia green (Actiengesellschaft für Anilinfabrikation, see pag. 153) extends very far into the red and, as can be seen from the last two illustrations of the table (III. Group), it can be used of a dark red filter of copper | ruby glass the infrared sun lines Z, X ,, X,. . . easily photograph. These two dyes are therefore also, when spectral recordings are concerned in the infrared part of the spectrum, do good service.

If we look at the dyes investigated in this section of the book and described with regard to their sensitizing effect, we see that it is easily possible to find a sensitizer for each spectral region that is compatible with it gives sensitized plates a high sensitivity. Table IV shows us the use of certain yellow dyes (see pag. 164) for the sensitization of bromosilver layers in blue-green, violet and ultraviolet. The heliographic panel V demonstrates the usability of different sensitizers for green, yellow and red, as well as for the subsequent infrared. As has already been noted, some of these dyes have found use in photographic practice, while others have been used by the spectral analyst should be of value to sensitize his dryplates to certain parts of the spectrum.

IV.

## SPECTRAL ANALYTICAL STUDIES ABOVE

### THREE-COLOR PHOTOGRAPHIC PRINTING.

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Spectral analytical studies of three-color photographic printing. Of

J. M. Eder.

(Presented at the meeting of the Imperial Academy of Sciences on July 2, 1902.)

The photographic three-color printing process, which is now widely practiced, still presents many difficulties in its photochemical part. There are various systems in use in which the photographic selection of the red, yellow and blue (respectively red, green and blue-violet) color components of a polychrome object by means of colored light filters which are inserted into the light path of the light image, with the simultaneous use of different types of sensitized photographic plates is made 1). The three-color printing system is mostly attributed to Young, Helmholtz, later Maxwell 2), which is followed by further training in actual three-color photography by Ducos du Hauron, Albert, H. W. Vogel and numerous other theorists and practitioners.

The most important class of photographic color synthesis includes color synthesis by subtraction (overprinting of yellow, red and blue inks: three-color collotype and autotype).

In spite of the fact that this area has been dealt with many times, one finds contradicting information about the basic chemical conditions in the production of negatives, even if one decides to use one and the same system of printing inks to be used. For practical reasons, the printing inks usually chosen are chrome yellow, madder or alizarin red and Berlin blue (so-called Milori blue), which corresponds to an old custom of printers and is motivated in the specialist literature 3).

However, it is always a matter of dividing the color spectrum into three zones using light filters, which approximately correspond to the primary physiological colors. The three different negatives, or print clichés, produced afterwards, are printed with printing inks which are complementary to the light filter colors that were used to produce the negatives.

1) cf. Eder: • Extensive handbook of photography », III. Vol., 5th ed., 1903, p. 693.

2) cf. G r e b e: "History of the three-color syntheses (" Zeitschrift f Reproduktionstechnik ", 1900, issue 9 and 10).

3) cf. Hl: «Die Dreifarbenphotographie», 2nd edition, Halle a. S., 1902.



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But if one analyzes the light filters proposed by the theorists 1) by means of the spectral apparatus, it turns out that in the photographic recording the color zones are cut off in one of the following three main forms:

a)

from Roth to D, then the other in size from D to incidentally F, immediately after that the third zone in blue-violet,

b)

or the spectrum is broken down into similar zones, but do not let them collide with one another, but rather select further spectral regions in such a way that they noticeably take hold in yellow and green and coincide (albeit with decreasing brightness) at the borders.

c)

or - you take the opposite path and make the three color zones so narrow that they remain between them in both the yellow and blue-green districts.

Since the theorists seldom corroborate their theoretical views sufficiently with practical collotype and autotype samples in their publications in three-color printing, while on the other hand the practitioners as a rule carefully keep secret those systems of color selection with which they achieve their excellent practical success, so for several years I have made three-color printing the subject of detailed investigations, which are carried out in parallel on the one hand in the spectral analytical and photochemical direction, and on the other hand empirically in the k. k. Graphic training and research institute in Vienna were carried out carefully comparing. Since these attempts lead to recognized three-color printing, the overall result of these studies appears to have progressed so far that the precise spectral-analytical definition of this working system that I undertook should contribute to the knowledge of the scientific basis of three-color printing.

Without going into the numerous series of tests that I made with the various light filters and types of plates, I want to characterize the spectroscopic properties of those optical and photographic aids that currently provide me with the best three-color prints (collotype and autotype), although I do not want to claim that these Results are final; for on the contrary I am made to believe that they can no doubt be improved considerably.

If we had an ideal panchromatic plate which is well sensitive to all rays of the spectrum, our matter would be considerably simplified, because one would only have to search for suitable light filters.

Unfortunately all of them are currently panchromatic. Plates imperfect; they have gaps in color sensitivity and show irregular maxima and minima in spectral photography. If separate plates sensitive to green and blue violet are used, similar conditions are found; for example, the plate sensitive to yellow should be sensitive to yellow, green and blue; Unfortunately, yellow sensitivity often dominates so strongly that you have to use a "damping light filter" which not only limits the relevant spectral zones, but also strongly attenuates or attenuates the incident color rays in certain areas (correction of the color effect by damping filters).

I have studied some of these phenomena carefully and will describe the connection between the color sensitivity of the photographic plate used and the spectroscopic properties of the matching light filters, as well as the regulation of these properties for the purpose of producing good three-color prints.

For these purposes the comparative spectral analysis of both the spectrum is necessary of the light reflected by the printing inks used as the quantitative determination of the absorbance

1) cf. Eder: «Comprehensive Handbook of Photography •, III. Vol., 5th ed., 1903, pag. 194 and 698.

tion spectrum of the light filter and finally the spectrographic impression of the color-sensitive plates used.

I deliberately left quartz apparatus aside for this series of experiments because my practical photographic control experiments were carried out with glass lenses. I also refrained from using the grating spectrograph, although I had started work with it 1).

Since the glass spectrographs are much easier to obtain than grating spectrographs for a possible repetition of these experiments, but on the other hand the obvious usability of the prismatic spectrum for purposes of three-color printing has been questioned several times, which did not seem justified to me, I considered it in the interest of generalizing the spectrographic investigation methods. It is desirable to ensure the relationships between the prismatic spectrum and the three-color printing. My glass spectrograph contained a triple

Fig. 1.

Compound prism made of glass (stone ax 2),

while my spectral apparatus for Vierordt's quantitative spectral analysis (Krs) only had a glass prism. It appears of interest to reduce the scale parts of the benzene spectral apparatus to full lengths in the same way

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as a curve and the course "

These curves can be compared on the one hand for the Krs universal spectral apparatus with a simple glass prism and on the other hand for advantageous triple glass compound prism (stone ax) for spectrographic purposes. Fig. 1 shows the slightly different one

Course of both curves 3). Although the

Millimeter scale

different spectral regions in something

Comparison of the dispersion used for the  
experiments different dimensions

Spectral apparatus. appear, the results of my subsequent work were always completely comparable. For the adjustment of such spectral apparatus to the wavelengths of light, in the interest of greater accuracy of the results, I used far more lines of more clearly normal specifications than are usually recommended in the textbooks. In addition to the Fraunhofer lines, I determined the position of the main lines of sodium and thallium, the magnesium spark spectrum, the spectrum of the lithium flame and the lithium spark (carbon with lithium chloride) Lead (spark spectrum) 4) and supplemented this with the spark spectrum of iron. The standards, which are somewhat confused and close to one another, leave behind one another

1) cf. p. 48, Part II of these treatises.

2) The exact description of this glass spectrograph with a glass compound prism can be found on p. 158, Part I of these treatises.

3) They are related to different zero points of the scale, therefore they are further apart. ') Cf. pag. 44, 1st part of these treatises.

J. M. Ed er.

can be easily disentangled if the main lines are identified from my spectrum photographs, Fig. 1, Plate II (heliographic table). In this spectrum, on a color-sensitive plate, the flame spectrum of sodium appears through the entire spectrum photograph, in the upper third the spark spectrum of an alloy of equal parts cadmium, lead and zinc, in the lower two thirds magnesium and iron spark spectra, the latter especially for the reliable determination of the woman nh of e rian lines G (Fe,) = 4308), L (Fe, A = 3820), M (Fe,) = 3727) does the best service.

The heliographic reproduction, plate II, Fig. 1, is also the connection of my previously recommended guide spectrum of Cd + Zn + Pb from the ultraviolet to the Roth given and completed.

If one works with light sources of a continuous spectrum, such as Auer, petroleum, gas, acetylene light, which is often very recommendable for investigations of absorption spectra, then taking photographs of the spark spectrum of my alloy is sufficient for orientation. This orientation is made easier with the help of the signature of the metal line inscribed on the Heliographe board. The magnesium spark spectrum is also characteristic for the greater part of the spectrum (corresponding to the Fraunhofer lines b1, b2, b3) and in this case, together with the blue magnesium line, provides good standards (cf. heliographic table, Fig. 1).

For the purposes of three-color photography, the spectral tests also had to be followed by samples using pigment colors. The relationships between the brightness distribution of light reflected in the solar spectrum and light reflected by pigment colors have been investigated for a few special cases and multiple data are available.

The yellow (in the Fraunhofer line D) in the solar spectrum is estimated by various observers 1) 9 to 31 times optically brighter than the spectral blue (for F to  $2/3$  G) and 21 to 87 times brighter than the darker spectral blue for G, while pigment yellow appears around 6 to 14 times lighter than blue in the yellow color range and yellow is 19 to 40 times lighter in the spectrum than red (for B to C), but appears only 3 to 7 times lighter in pigment colors 2).

Since the relative brightness distribution of the grating and prism spectrum in yellow and blue is again different, it follows that all these experiments cannot give directly comparable results for the photographic value of the colors.

It is the spectrographic property of the color-sensitive plates to determine the physical property of the light filters and to try their effect in the reproduction of pigment colors in order to find the experimental basis for the interrelationship of the various aids to the practical successes in the production of three-color photographs.

Relationship between quantitative spectral absorption of light filters and the photographic effect in multicolor photographs.

The knowledge of the qualitatively determined absorption spectra of light filters does not lead to an interpretation of their function in multicolor photography, because the extent of the color zone which becomes photographic depends on the exposure time and the respective light intensity. This results from the consideration of any of the absorption curves shown below (Fig. 5, p. 14).

1) After Vierordt («Poggend. Annal.», Vol. CXXXVII, 1869); Crova and Lagarde ("Compt. Rend.", Vol. XCI I, 1881); Mace de Lepinay and Nicati ("Annal. De Chim. Et Phys.", Vol. XXIV, 1881; Vol. XXX, 1883); Abney ("Philosopher. Transact. Of the Royal Soc.", London 1886); for other treatises see Edler's Jahrbuch der Photographie.

2) Rood: "Theory scientifique des couleurs", Paris 1881; Schenk: "Pfleger's Archive", Vol. LXIV (1896); Martius: «Contributions to Psychology and Philosophy», I, 1896; Rivers. Journal of Physiology, 1897; C. Bonacini: «Società fotogr. Italiana», 1902, p. 91.

With a short exposure only the brighter parts of the spectral region penetrating the filter will come into their own (corresponding to a narrow band of colors); with longer exposure, the heavily subdued color zones will also have a photographic effect. So after a longer exposure (or stronger light intensity) a wider band of colors will come into effect, that is, more extensive spectral regions will produce a photographic effect than with a short exposure.

I tried to remove this uncertainty in assessing the effect of the light filters by relating the photographic effect of the light filters numerically to their quantitative spectrum. This way leads to a good characteristic of the light filters used in three-color printing.

In reproduction photography (painting, etc.) one always has to expose so abundantly behind light filters that the details in the shadow areas become clear. The limit of overexposure (limit of the maximum permissible exposure time) begins when the brightest lights in the negative are just about to separate or not yet completely blur into one another. Exposure and development may not be carried further than until the densest areas in the negative (depending on the reproduction technique) have attained "blackening" 2 to 3 (on average  $2 \cdot 5$  1). The brightest color zone of a light filter will therefore be allowed to act in normal negatives until the photographic blackening  $2 \cdot 5$  has been reached and then see how far the half-attenuated color zones still had a photographic effect under these conditions. This process, however, also puzzled me. The results are not too constant, because a certain latitude in exposure and development noticeably influences the gradation of the photographic density; but at least these observations allow a better insight into the function of the photographic light filter than one had hitherto.

My manifold experiments with yellow, green and blue filters have shown that with very short (practically hardly sufficient) exposure the light filters cut off completely where the transmitted light is weakened to 30 to 40 percent 2) 3). In the case of medium exposures, those spectral regions where the remaining light intensity is 10 to 20 percent 4) come into effect. Where the light filters have a light intensity of about 10 percent, you have to set the approximate limit of the photographic light transmission of the color filters at normal exposure time. In the case of very long exposure (at the limit of overexposure), a moderate photographic effect also becomes apparent in those color areas where the light intensity is only about 5 percent 5); Admittedly, the photographic blackening of the negative is only slight at these points, for example  $0 \cdot 4$  to  $0 \cdot 5$ , when the photographic blackening  $2 \cdot 5$  is reached at the points of greatest light intensity.

It is always assumed that the photographic plates have good sensitivity at the relevant points and that the points of light filter attenuation do not coincide with the minimum sensitivity.

One can generally assume that with the copious exposures used in reproduction photography, the strong light image begins where the constant light intensity is 20 percent of that which is effective at the points of maximum permeability of the light filter

1) cf. p. 48, 11th part of these treatises.

") Corresponding to the extinction coefficients (according to V i e r o r d t) =  $0 \cdot 52$  to  $0 \cdot 39$  (that is the negative logarithm of the remaining light intensity).

3) Set the point of greatest permeability = 100. · 1) Corresponding to the extinction coefficients  $1 \cdot 00$  to  $0 \cdot 70$ .

5) Corresponding to the extinction coefficient  $1 \cdot 30$ , that is the blackening corresponding to a very delicate semitone.

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arrives; at 10 percent light intensity a halftone is created behind the color filter, while at 5 percent light intensity the only very delicate halves that are practically no longer effective for three-color printing are created in the photographic negative.

In such experiments one must take into account the reflection spectrum of pigments (together with the solar spectrum) in order to adapt the experimental conditions to the actual three-color photography.

For this purpose I put together a number of printing inks, which are chemically and physically well defined and whose reflection spectra encompass the entire ~ 1 visible spectra, in a sample color table (see Plate I).

Reflection spectra of printing inks, which can be used for three-color printing or for the production of sample color tables.

For the present study, I chose a color table with vermilion, chrome yellow, Schweinfurtergr, ultramarine blue, methyl violet varnish and underneath put the currently used normal colors for three-color printing, that is madder varnish (in the enclosed sheet I varnish from Alizarin red), milori blue, that is particularly nuanced Berlin blue, and chrome -Fig. 2. yellow. The black border, along with the white paper ground, represents the deepest blacks and lightest white spots of the original, while the graduated collotype scale (plate I) the gradation of the photographic blackening

A a B C D E b, F G h HK L

reveals. I examined the reflections<sup>2</sup> spectra of the colors of my polychrome test panel (plate I) as chrome yellow as the normal colors f Dreia a BCDE b1 FG h HK color printing and some other similar pigments<sup>3</sup> more closely and represented them graphically in Fig. 2 and 3. Von Gelber Lack Colored light reflected from printing inks (pigment with LeinG h HK varnish) always contains white light mixed in, which makes the perception of the color spectrum dominated by the pigments somewhat reflective of printing inks. difficult; in the case of cinnabar, which does not completely cover, some white light also shimmers through from the paper. I tried to make these influences harmless by observing the spectra coming to the dyes by making a Vierordt double slit on the spectral apparatus, into which one half of the slit allowed the light reflected from the colored printed paper surface to enter, the other half white, reflected light Throwing light by means of prisms and by narrowing the

Orange, yellow and yellow to methyl violet

approximately to the Fraunhofer A a B C G h

HK L Lines E to F. Already in Gr

at), = 542 the light reflector is 4-1

xion weaker, even weaker at). = 500 to 480. Blue-violet alizarin red lacquer

and ultraviolet become strong from the reflection spectrum of printing inks. sorbed. The green paint, here represents from quercitron bark 1), is

Column dampened accordingly. One can almost certainly estimate the continuous spectrum of white light that is part of the dye spectrum and then with more certainty recognize and sketch the color spectrum that is characteristic of the dye.

In this way I graphically presented a number of reflection spectra of printing inks, Fig. 2,

~.

No. 1 to 4 and Fig. 3, No. 1 to 4. These curves correspond as closely as possible to the observations made in this way; However, it should be expressly noted that only the practically dominant reflection spectrum of the pigments in question, apart from the admixtures of diffuse reflected light, is only shown qualitatively (schematically). The curves are easy to understand; the bright parts correspond to the shining parts of the reflection spectrum. Zinnober (No. 1) Fig. 3. The spectrum absorbs green light on one side from approximately blue to violet; Thin layers of paint, however, let some white shimmer through from the paper. Is chrome yellow

a pretty good body color;

As a blue green in spite of this, in the case of thin layers, the absorption spectrum can also be seen in the light falling through

Ultramarine

determine, as well as the ana

Log reflection spectrum (Fig. 2, A a B C D E ~ F: ~ ~ ~ ~ = G: ~ ~ ~ ~: h ~ H ~ ~ ~ ~: K: ~ L ~ No. 2) . The absorption in Roth is low; Chrome yellow reflects pretty well red, then very well

a glaze paint; even in thick layers it lets more green through than chrome yellow; the layers printed on white paper reflect well red, orange, yellow and yellow-green, Fig. 2, No. 3, even up to). = 506 light is still reflected, so that it has more green tint than normal chrome yellow.

As a red h 1 a c k gives the madder paint spectrum, that is, it has good red permeability (glazed); the absorption band starts at). = 602, maximum at). = 592 up to around 500, decreases at). = 500; in blue it is quite transparent light of the wavelength i, = 486, even more is light from). = 470 from down to blue-violet and ultraviolet transmitted (Fig. 3, No. 4).

1) The "yellow varnish" of the trade is a very differently composed printing ink. Quercitron lacquer is not infrequently made with tar paints, and there are even "yellow lacquer paints" on the market which are made entirely from tar paints.

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Schweinfurtergr reflects only a little red and orange, not much yellow (up to D), very good Gr and blue gr up to F, while blue is weakly reflected (Fig. 2, No. 4). The Schweinfurtergr is a poor printing ink and is not used for color printing; However, it is particularly suitable for the test color table because the more or less correct reproduction of the same in comparison with chrome yellow and ultramarine blue is a very good feature in photographic test exposures (criterion for the usability of photographic plates and light filters for three-color printing) and is better than that most aniline dyes can be used for the photographic sample panel.

The absorption spectrum of Methyl violet is at least qualitatively well known. The spectrum of the methyl violet lake (Fig. 3, No. 3) corresponds to the spectrum of this dye. Incidentally, I have also examined this spectrum by means of quantitative spectral analysis (see below), since it had not yet been adequately studied in this direction. Methyl violet varnish is not true; Nevertheless I chose it because its reflection spectrum is relatively sharply limited and it therefore provides a good test color for photographic reproductions (in addition to ultramarine blue, No. 2).

The absorption and reflection spectrum of the Mithridate (Berlin blue) is shown in Fig. 3, No. 1. Red to orange is swallowed; in the case of weak layers, permeability occurs in the light green; thicker layers dampen the whole of the green to blue, as the dotted curve indicates.

Painted and printed colored surfaces always reflect mixtures of colors, especially colors from the neighboring zones of that part of the spectrum whose main color they have; For example, chrome yellow not only reflects pure spectral yellow, but also orange-red and green, which are the spectral colors that are adjacent to yellow. Green color pigments reflect yellow and light blue and often a zone in the outer red. Most purple pigments reflect not only blue but also considerable amounts of light red etc.

This property of the painters and printing inks makes it very difficult to separate their photographic effect in an appropriate way by means of suitable light filters and color-sensitive plates and, on the other hand, explains practical experience that they are badly combined. Closing color filters, which leave green in the spectrum, but with three-color printing still allow all pigments in a painting to more or less achieve a photographic effect. It is here. For the sake of completeness, reference is made to the various brightness stimuli which pigments of different colors exude on the human eye<sup>1)</sup>, which relationships are made more complicated by the occurrence of the Purkinje phenomenon.

Spectrographic examination of three-color printing of suitable photographic plates.

The photographic plates of various preparations to be discussed in more detail here are those which I found in practical experiments over several years at the k. k. Graphischen Lehr- und Versuchsanstalt actually gave usable results and tried them out. They therefore deserve to be described in more detail in order to gain the material for the scientific study of the three-color process on the basis of practice.



For the yellow printing plate, negatives come into consideration which were created under the influence of the blue-violet rays. Large rays are no more allowed to have an effect than yellow and red rays.

Accordingly, wet iodized silver collodion plates, iodobromide collodion plates, silver bromide gelatine and chlorosilver gelatine plates come into consideration, the main sensitivity of which is blue and violet.

1) Abney «Investigations • (Eder: <Ausführliches Handbuch der Photographie», III. Vol., 5th ed., 1903, pag.283).

The wet Iodized silver-Collodion plate ("wet Collodion process" with acidic iron vitriol development 1) gives the violet and blue up to  $\lambda = 437$  with normal exposure (in the sense of my erosion) and works itself on the border of the Overexposure within the limits established by photographic practice does not suggest much further against light blue or blue-green. Since the photographic practice with three-color printing shows that one can produce usable yellow printing negatives with such plates, we have found a standard in the spectral zone) ... = 437 up to the end of the violet, which counteracts the limit of permissible cutting of the color ribbon results in the more breakable end and is clearly shown in Spectrum No. 16, Plate II (solar spectrum, glass spectrograph). Further advance of the border against the outer violet brings with it an unfavorable success in three-color printing.

Therefore, Chlorosilver plate in step 1 with chemical development 2) despite their dominant violet sensitivity for three-color printing, because they are not sensitive enough in light blue. With "normal" exposure they give the spectral effect depicted in Spectrum No. 14, Plate II, whereby the insufficient sensitivity to blue is evident. However, one must bear in mind that in the event of overexposure the spectral effect can gradually increase into blue up to G, so that with increasing exposure, wide color areas come into effect and one easily loses control of the color selection when using chlorosilver gelatine. Incidentally, chlorosilver gelatine is generally too insensitive for negative photography, so three-color printing is no longer an option.

Pure iodized silver collodion is also not very sensitive and is exceeded by a multiple of iodine bromocollodion 3) and the sensitivity not only extends relatively further to light blue, corresponding to the addition of silver bromide (see no.15, plate II ), but also the absolute sensibility of the blue-violet band, which is inherent in the iodized silver itself. The iodobromocollodion therefore offers advantages, and the question arises as to how it relates to the selection of colors. Empirical test series showed me that even wet iodobromocollodion plates with a large amount of iodide give practically usable yellow print negatives without the use of any color filter. The photographic "normal" exposure as well as the incipient overexposure always provide the green or blue-green practically correct, because the weak bromosilver band in the light blue is not too widely available, in cases which are carried out correctly due to the dominant iodine sensitivity are. In the case of Collodion with a dominant bromide silver content, however, there would be a risk that the light effect would advance too far into the blue; So you have to choose iodobromocollodion with a considerable amount of iodine 4).

Silver bromide gelatin is very sensitive to violet to light blue when exposed to ample light, but even up to the blue green. In this case, too, the effect increases (analogous to the silver chloride,

but in contrast to iodized silver) gradatim into the green, with very strong exposure up to yellow at the Fraunhofer line D, so that with increasing exposure one indeterminate color selection

(clearly noticeable in the reproduction of paintings) in front of him. At least one can assume, that the spectrum photograph of the average normal exposure shown in No.

11, Plate II

in the sense of my delusions (see before) The empirical test series in three colors

Prints taught me that on the bromide-silver gelatine plate the blue part of the pigments (Schweinfurter 's) Eder: 'Receipts and tables for photography and reproduction processes, which at the k. k.

Graphischen Lehr- und Versuchsanstalt in Wien are applied », 5th ed., 1900, pag. 25.

2) cf. pag. 126, Part II of these treatises.

3) That at the k. k. Graphic teaching and research institute used Jodbrocollodion (Eder: «Recepte und Tabellen») is 2 to 3 times more sensitive than pure Jodcollodion.

4) See the mixing ratio communicated afterwards.

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Eder. 10

gr) acts too strongly and then no good yellow printing plates are produced. These printing plates would deliver too little yellow, the yellow plate printed at the bottom would be too empty of yellow; However, in terms of printing technology, it should contain plenty of yellow, rather too much to give a good "conclusion" in terms of color. This explains why yellow printing plates, in which spectral regions that are too broad (blue-green to violet) have a photographic effect in the negative, are usually practically inferior to those made with yellow printing negatives, which were only produced by means of a narrow blue-violet zone. were manufactured. Practical tests over several years have shown me that silver bromide gelatine plates for three-color printing give the best results if a violet filter is switched on in the beam path, which inhibits the presence of the spectral effect against Gr even in the event of overexposure, for example like the spectrum photographs shown (Plate II, No. 6 and 12) show. The process, which is already widely used in the practice of three-color printing, of switching on the violet filter on bromide-silver gelatine plates, is justified and only makes quantitative ones

In the case of silver bromide gelatine, the gradation is not affected by switching on a violet filter, but only the light is attenuated to different degrees, which in practice results in exposure times of different lengths and can be seen from FIG.

Green printing plates, which are to be used for three-color photography for the production of the red printing plate, are very difficult to produce with the correct effect. The spectro-. The graphic sensitivity band in the size of yellow should rise next to the Fraunhofer line D and run vigorously and continuously to the level of blue as far as F, as the spectrum photographs indicate in two variants (Plate II, No. 7). Unfortunately, the erythrosine plate mostly used for this purpose (probably still the best) is not very sensitive in the blue and too very sensitive in the yellow, as the spectrum photography (plate II, no. 10) clearly and characteristically shows

1) cf. p. 48, Part II of these treatises.

2) See my "Jahrbuch f Photographie und Reproductionstechnib, 1901, pag. 56.

3) cf. p. 48, Part II of these treatises.

4) The representation of the blackening curves (with constant exposure time) was done according to my treatise on sensitometry; See p. 48, Part II of these treatises.

5) cf. pag. 48, 111 and 126, Part II of these treatises. Fig. 4.

Silver bromide gelatin with water filter

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with methyl violet filter

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g with acid violet filter:

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130 100 70 10 notes

Blackening curves of silver bromide gelatine plates behind violet light filters.

to carry out spectral analytical characterization of such suitable filters (see later). Connecting b 1 au e n copper oxide ammonia light filters always gave me poor results (see later). On this occasion I come to the requirement that I have expressed 1), confirmed by one of the most experienced specialists in three- color photography (Dr. J. Husnik in Prague) 2) which multicolor printing is important: the Partially negative have approximately analogous gradation. It was therefore of interest to investigate whether the upstream connection of the violet filters mentioned influences the blackening curve 3) sensitometrically. A sensitometric sample (S\_cheinerSensitometer, amyl acetate) gave the result shown graphically in FIG. 4 4); the characteristic blackening curve runs behind the water filter, methyl violet filter (1: 10000) and acid violet filter (1: 2000). almost parallel, that is, that expose so abundantly that

the blue-green has a strong effect and at the same time attenuates the yellow-green with blue or gray light filters. The correct execution of this process requires precise spectroscopic examination of the filter, the results of which are described a little later.

Most of the orthochromatic plates on the market (e.g. Schatte r a's orthochromatic plates) are such erythrosine plates. For my experiments, I made them myself according to the following, at thek. k. Graphic teaching and research institute called the elaborated regulation:

Silver bromide gelatine plates are bathed in diluted ammonia (100 cm<sup>3</sup> water and 1½ cm<sup>3</sup> ammonia) for 2 minutes, then immediately placed in a dye bath of 100 cm<sup>3</sup> water, 6 cm<sup>3</sup> erythrosin solution (1: 500), 1½ cm<sup>3</sup> ammonia for 2 minutes and after draining in vliiger Darkness dried.

The color sensitivity (especially yellow-green) of the erythrosine plate I have described in detail in earlier treatises, as well as my observations and the course of the blackening curve 1). Eosin or related dyes, which further impart the sensitizing band to silver bromide against green, would theoretically be more correct than erythrosine. Unfortunately, the overall sensitivity of the eosin plates is lower, especially at the point of the minimum in the blue grime, so that the erythrosine plate (despite the strong damping filter) needs shorter exposure times and I stay with the erythrosine plate for the time being. The correction method by means of larger light filters examined with spectroscopic precision is very characteristic of works of this kind and I have therefore examined them carefully (see later).

Silver bromide collodion emulsion colored with eosin silver (from tetrabromofluoresce "in sodium) or ethyl eosin, phloxin, etc. is cheaper than eosin-bromosilver gelatin. Plate II, No. 4, shows the effect of the solar spectrum on bromosilver collodion with tetrabromo-fluorescei; the effect continues againstD). Fluorcsce "insilber is very sensitive in size

(see Spectrum photography, Plate II, No. 5), but too little for yellow-green, so not enough for three-color printing; With all color-sensitive plates with a similar course of the sensitizing band in the solar spectrum, it is possible to photograph large pigments with the same photographic opacity of the negatives, but not yellow ones.

Monobromofluorescence behaved very well in bromosilver collodion, and I stayed with this preparation, the sensitivity of which in the dark green approaches that of fluorescence, but in the yellowgreen it is less powerful than eosin, which is worthwhile

I found 100 cm<sup>3</sup> bromosilver collodion (Albert's emulsion) mixed with 10 cm<sup>3</sup> alcoholic monobromo fluorescence (1: 500 2) as the best prescription for the size-sensitive collodion emulsion. Sometimes a small addition of cyanosine or ethyl eosine was also beneficial.

The plates are poured with it, after solidification immersed in a weak silver nitrate bath 1: 500 (not acidified), after a few minutes exposed while still wet, best removed with water and developed with the well-known alkaline hydroquinone-3) or glycine developer 4).

These monobromo fluorescent plates must also be combined with green filters in order to force the photographic effect (similar to that of erythrosine plates) more against blue green;

1) cf. p. 48 and 126, Part II of these treatises.

2) Obtained from the Badische Anilin- und Sodafabrik in Ludwigshafen.

3) The hydroquinone developer with the following composition is particularly suitable for screen negatives (Tschene: "Photographische Correspondenz", 1903, p. 357):

Lung A: 10 g hydroquinone, 20 g sodium sulfite, 400 cm<sup>3</sup> water; Lung B: 10 g potash, 100 cm<sup>3</sup> water. For use, 1 part of Lung A is mixed with 2 parts of Lung B. 20 drops of potassium bromide solution 1:10 are added to 100 cm<sup>3</sup> of finished developer (1903).

4) The same glycine potash developer that is commonly used for brown silver gelatine Eder: («Receipts and tables»,

) 900, pag. 14 and 35).

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There are weaker damping filters here; Occasionally a short post-exposure without a green filter is in order to correct wrongly too little yellowing; The combination of monobromofluorescence with a tetrabromofluorescence derivative (cyanosine or ethyl eosine) has served me well in difficult cases.

All of these gr-sensitive plates show a notable blue-violet sensitivity (intrinsic sensitivity of bromine silver), which must be switched off with a suitable yellow filter. This process is particularly important and must be precisely controlled (see later).

The B 1a druck p 1a t t e in three-color printing is produced by means of a negative produced behind an orange filter, for which red-yellow sensitive plates are used. Such plates should be sensitive in the red at least from the Fraunhofer line C to D in yellow to the border of light yellow green, as in Plate II, No. 3 (bromosilver collodion with the ethyl violet indicated by E. Valenta 1), shows. According to my experiments, there are still sensitizations whose maxima lie between C and D (Plate II, No. 3), if the sensitization increases with copious exposure to C or beyond, which, for example, is the case with that given by E. Valenta Wollschwarz 2) and nigrosines that I first mentioned and what also with von Schatte A red-sensitive plate produced at the factory in Vienna takes place behind orange filters (see Plate II, No. 8), where the effect extends even to the solar spectrum. On the other hand, I found that there was very little sensitization against red orange, as stated in No. 2 (A 1b er's bromosilver collodion with commercially available color sensitizer), so that, for example, cinnabar is poorly represented in comparison to chrome yellow. I found these limit values against the less frangible side of the spectrum in my experiments and repeated attempts have confirmed them, although in literature and practice one finds several times recommended for Roth less well sensitized plates. The limit of the color effect towards the more breakable end can sometimes extend towards light yellow (roughly as Plate II, No. 8, suggests) and careful quantitative spectral analytical determinations taught me how useless red light filters are, which are in the region in front of D in Cut off the orange (see later).

I sensitized my red-sensitive drying plates with wool black, which gives the best results in the following way.

Roth-sensitive Wo 11 black bromine i l berge l a t i n e p l a t t e n. First, ordinary silver bromide gelatine plates are bathed in a lung of 100 cm<sup>3</sup> of water, 1½ cm<sup>3</sup> of ammonia for 2 minutes; then they are immersed in the sensitizing bath: 5 cm<sup>3</sup> wool swab (wool black 4 B of the Berliner Actien-Gesellschaft for aniline fabrication [1: 500]) or dianil black N (Meister, Lucius, Bring & Comp.), 100 cm<sup>3</sup> \ Wet, 1½

cm<sup>3</sup> ammonia 3). Bathing time: 2 minutes; two filtered baths are used one after the other, each lasting 2 minutes. One dries in complete darkness.

While this wool black plate with orange filter gives good results for three-color collotype printing (Schattera's "red-sensitive" plate behaves in a similar way), an autotype is recommended (zinc or copper etching for letterpress printing) the following red-sensitive Collodion emulsion: 100 cm<sup>3</sup> A 1b er t'sche Collodion emulsion, 2 cm<sup>3</sup> ethyl violet (1: 500), 5 cm<sup>3</sup> monobromo fluorescent

(1: 500). The plates are poured with this and, after solidification, immersed in a silver bath (1: 500) - not acidified - and exposed while wet 4). I added the monobromofluorescein because

1) "Photographische Correspondenz", 1901, p. 37.

2) "Photographische Correspondenz", 1900, pag. 102. Obtained from the Actiengesellschaft fAnilinfabrikation in Berlin.

3) Some silver bromide plates create a veil with ammonia in a paint bath; then this addition of ammonia is omitted and the plates are clearer but less sensitive. The ammonia pre-bath is then all the more necessary and must not be left out.

4) After exposure, water is best removed and the plate, like the fluorescent plate, is developed in an alkaline manner.

the ethyl violet plate then has better overall sensitivity 1) and gives purer layers; the increased sensitivity due to monobromo fluorescence does not come into its own behind orange filters and is not the ultimate goal of this addition.

Emulsions freshly mixed with these dyes sometimes work cloudy 2), which improves by itself after 1 to 2 weeks. The plate produced as above can also be bathed in very dilute acetic acid after exposure and before developing, the veil being destroyed 3). Acidification before exposure is not recommended because of changes in the sensitizing dye.

In the further course of my work, I investigated the connection between such color-sensitive plates and suitable light filters and their effect in the multi-color photography of pigments.

Quantitative spectral analysis of some types of light filters.

To determine the spectral analytical properties of light filter types, I have determined the absorption and the extinction coefficients 4) of some of them.

It is by no means permissible to draw conclusions about its usability from the beginning, the respective end of the absorption spectrum or the position of the absorption minimum of a light filter.

There are many dyes that are not sufficiently transparent for any zone of the spectrum and measurably attenuate the light even at the point of greatest permeability. A mere inspection of the absorption spectrum easily escapes the observer, but comparative photographic exposure experiments or, better still, quantitative light absorption measurements make these influences very noticeable.

An example should make this clear: Acid violet 4 B extra (Farbenfabriken formerly Bayer & Co. 111 Elberfeld) is a brilliant violet dye, similar to methyl violet, but much more light-resistant. It's easy to make a good purple light filter with it if you put it in water for about 1: 2000.

This light filter cuts off genend for three-color printing and that canthe qualitative light absorption is limited in a very similar way as with methyl violet (1: 10000), which can be seen in nos. 6 and 13 of the heliographic plate II. Nevertheless, a silver bromide gelatin plate needs a much longer exposure behind acid violet than behind a methyl violet filter delimiting the same zone (see FIG. 4).

The reason is that in the acid violet the cut-out spectral zone is not fully transparent, but is partially strongly attenuated (but not in the case of methyl violet), which is not noticeable in qualitative optical samples, but in practical photographic comparative exposure tests 5) or by means of quantitative spectral analysis.

- 1) First shared in my treatise: "System of the sensitometry of photographic plates", III. Division; cf. p.126, Part II of these treatises.
  - 2) Originally I colored the emulsion with larger amounts of ethyl violet, after which the emulsion tendsto be more foggy than with the small amount of dye given above.
  - 3) The addition of a little acridine yellow also has an anti-haze effect (1903).
  - 4) In the sense of Vier o rd t's: "Use of the spectral apparatus for the photometry of absorption spectra", 1873; also "The quantitative spectral analysis", 1876; cf. Traub e: "Phys.-chcm. Methods », 1893; Krss: "Colorimetry and quantitative spectral analysis", 1891.
- ) The sensitometer curves shown in FIG. 4 also give (based on Seheiner degrees) the picture of the different strengths of the photographic effect of the light when the light filters in question are switched on.

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Suitable violet filters for the production of the yellow printing plate using bromosilber gelatin e.

Ordinary silver-bromide gelatine plates cannot be used without further ado for three-color photography, since their intrinsic sensitivity extends too far to blue-green (cf. the photography of the solar spectrum, plate II, no. 11). You therefore have to switch on a violet filter when taking a picture to attenuate the blue grime and then get good negatives for the yellow printing plates, as they are on the

k. k. Graphic teaching and research institute with particular success for three- and four-color collotypeprinting

be used. As a normal light filter f, FIG. 5.

Yellow printing plate corresponded best to a methyl · ~ ----,-- 0 · 8, .. violet filter with a concentration of 1: 10000 in one thickness

• • • & • O • O of 1 cm. The commercial varieties of methyl violet and

• • •

...

their coloring power change strongly, so that the light filter is not characterized enough with such a recipe. Therefore I determined the optical properties of such a methyl violet filter 1), which has proven itself in my experiments, and found the following extinction coefficients. The result is the absorption curve of my methyl shown graphically in FIG. 5, No. 3, about.2

o · •, violet light filter (1: 10000); here it is the  
waves0x0

•., Lengths of light and the associated  
extinctionsC.

"coefficients with their exact numerical values entered  
-;;;" "wear. Unfortunately, the methyl violet lungs bleach

~

"

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"0 C in the light for several weeks (apart from  
colors0

changes due to chemical reactions) and lose

~

C

.

much of their color intensity. Such a practical one

~

According to my measurements, methyl violet filters that had already become unusable had the following light intensities and extinction coefficients: If one compares my finding that copper oxide ammonia or similar light filters (the determination of the absorption of copper filters,

see my treatise: «System of sensitometry photo

, ..

graphic plates », III. Department) according to

my ver0 · 8

0 · 8 f yellow printing plates also look for the

bluegrassO••



too little, one also compares the absorption curve of the good methyl violet filter (1: 10000, see Fig. 5) with the curve of a light filter with stronger copper oxide ammonia, which still absorbs too little at F 2) (see J; fig. 5, curve No. 4) so are with it

2) Comparative practical tests of color synthesis (based on the printing inks: chrome yellow, Krapproth and Berlin blue) showed that the copper oxide ammonia light filters, even in large concentrations, only serve their purpose when necessary, for example a lung of 30 g of crystallized copper vitriol, Ammonia and water, made up to a volume of 1 l, a deep blue light filter, which in most cases allows too much of the border region of the blue-green to pass through and therefore usually provides a yellow print negative with a little too little coverage. Therefore, I believe I am justified in designating such a copper filter as the outermost limit of a blue filter for bromosilver gelatine, the absorption curve of which is characterized by quantitative spectral analytical determinations by the above figure.

(30 g bysl I (i., Pfe11'1trtol, 1000 cml Wn'le, see Ammonlllr:

Methyl violet 1: 10,000 (normal light filter for gelatin

plates).

Scala 1 wavelength 1 luminous intensity extinction • nscoefficient Scala 1 wavelength 1 1  
luminousintensity extinction coefficient

7 to 7¼ 7¼ 7½ "7½ 7¾" 7¾ 8 "8 8¼" 8¼ 8½ "8½ 8¾" 8¾ 9 "9 9¼" 15 „ 15¼ 15¼ 15½ "15½ „ 153/1 15¾

16" 16 16¼ "694 to 683 683 672 "672 662" ":" 662 653 "653 644" 644 635 "635 626" 626 "618 618 610"

492 489 "489 486" 486 483 "483 480" 480 476 - "0x88 0x05555 0 77 o 1135 0 65 o 1811 0 59 0  
2292 0

46 0 3373 0 35 0 4559 0 18 0 7474 0 07 1 1549 complete absorption --0 · 05 1 1 · 3010 10 · 08  
1 1 ·

0969 16¼ to 16½ 10½ 16¾ "16¼ 17" 17 17¼ "17¼ 17½" 17½ 17¾ "17¾ 18" 18 18¼ "18¼  
18½" 18½ 18 "/" 18 "/" 19 "19 19¼" 19¼ 19½ "191 /, 19¾" \_ 476 to 473 473 470 "470 467"  
467 464 "464 461" 461

459 "459 457" 457 454 "454 452" 452 449 "449 447" 447 444 " 444 442 "442 440" from then  
onwards 0

· 11 0 · 9586 0 · 17 0 · 7696 0 · 21 0 · 6778 0 · 28 0 · 5529 0 · 32 0 · 4949 0 · 36 0 · 4437 0 · 41 0 · 3872 0 ·

47 0 · 3279 0 · 55 0 · 2596 0 · 65 0 · 1871 0 · 77 0 · 1135 0 · 84 0 · 0757 0 · 92 0 · 0362 0 · 96 0-0177

completely permeable

Standards are given, which will provide good reference points for further determination of other types of light filters.

Iodine bromine-Collodion plates for yellow printing negatives do not need a violet filter. F. Dreifarben - Autotypie is best suited iodobromo collodion with abundant iodized salt. 7 g iodine cadmium, 3 x 2 g iodine ammonium and 1 x 2 g bromine ammonium are placed in 175 cm<sup>3</sup> of alcohol and filtered.

To produce negative collodion, 1 volume of the iodizing liquid is mixed with 3 volumes of 2% crude collodion. The Collodion layer is silvered in a 10% silver bath. Iron vitriol acid acidified with acetic acid

1) serves as the developer.

Methyl violet filter. (Concentration 1: 10,000. -Bleached in the light.)

Scala wavelength 1 extinction light intensity coefficient 1 Scala 1 1 wavelength 1 light intensity 1 extinction coefficient -

7 to 7¼ 666 to 655 - 12¼ to 12½ 507 to 502 0 · 08 1 · 0969

711 well through, 4 7½ 655 645 - "" casual 7½ 7¾ 645 635 - "" f Roth 12½ 12¾ "1 ! ¾ 13" 502 497 "497

492" 0 · 10 o · 17 1 · 0000 0 · 7696

7¾ 8 635 625 - "" 13 13¼ "492 488" 0 · 21 0 · 6778

8 8¼ 625 616 0 · 31 0 · 5086 "" 13¼ 13½ "488 484" 0 · 28 0 · 5529

8¼ 8 ½, 616 606 o · 13 0 · 8861 "" 12½ 13 48 "484 480" 0 · 37 0 · 4318

8½ 8¼ 606 597 0 · 03 1 · 5229 "" 13¾ 14 "480 476" 0 · 39 0 · 4089

597 to 517 strong absorption tape up to size 14 14¼ "476 472" 0 · 41 0 · 3872

11¾ to 12 517 to 512 0 · 03 1 · 5229 14¼ 14½ "472 468" 0 · 52 0 · 2840

12 12¼ 512 507 0 · 06 1 · 22191 1 1 "" 14½ 14¾ "468 465" o · 78 0 · 1079

(According to my more recent experiments made in May 1903 2) the ultraviolet, which passes through the methyl violet filter almost without weakening, can cause defects in three-color printing. The ultraviolet is switched off by adding 0 · 05 ° / 11 esculin to the methyl violet. The addition of 0 · 05 to 0 · 1 ¼ Ae ~ culin extends the exposure time from 1 to about 1¼-)

1) S. Eder: • Receipts and tables for photography and reproduction processes, which were carried out at the k. k. Graphic teaching and research institute in Vienna to be applied •, 1900, pag. 25.

2) S, Part II of these treatises: "On the sensitometric printing of ordinary and orthochromatic photographic plates."

J. M. Eder.

Grfilter for the production of the red printing plate.

I have tried a large number of the extraordinarily varied size filters that have been proposed so far (nickel, copper salts, malachite, acid, combinations of the same with yellow dyes, bichromate, etc.) and

have referred to both yellow-sensitive silver bromide gelatin and silver-bromide collodiums that are sensitive to yellow.

Erythrosine bromide gelatin plates and suitable gr filters.

For the purpose of color photographic printing I use erythrosine plates sensitive to yellow (see above) or similar orthochromatic plates colored in the emulsion itself (for example from Schattera in Vienna), which usually show better gradation in the lights than bathed plates.

You need strong correction light filters 2), the optical properties of which have the greatest influence on success. The light rays must be attenuated on the less breakable side of the spectrum, from orange- yellow to yellow-green (region from Fraunhofer line C to D), so that the spectrophotographic image is on an erythrosine plate (plate II, no. 10 ) designed in the sense of plate II, no. 7, that is, the sensitization tape is pushed from yellow to blue. Such effects can be achieved, for example, with mixtures of Janusgr 3), with yellow dyes (such as auramine 4), as curve 2 in FIG. 5 indicates. The upper curve in this figure indicates the sensitization curve of the erythrosine bromide silver gelatin plate; the graphical representation of the absorption spectrum. Janusgr auramine (lower curve) shows a maximum thereof transmitted light, where the sensitivity of the erythrosine plate is at a minimum, and a spectrum photograph is obtained by combining the two, in which the main effect extends to Gr, as shown in Plate II, No. 7.

One can work well with such a system in three-color printing, as I have already indicated earlier 5), but the filter subsequently showed many disadvantages: it is not completely transparent at any point in the spectrum (see Curve 2, Fig. 5 and see the following table), therefore needs

Auramine (1: 15,000).

Scale 1 Wavelength 1 Light intensity Extinction coefficient 1 Note

14 to 14¼	14¼	14½	"14½	14¾"	143 /,	15	"15	15¼"	151 /,	15 1/ 2	"151 /,	15' /."	158 /,	16	"508 to
504	504														
500"	500	496	"496	492"	492	489	"489	486"	436	483	"483	480"	0x96	0x82	0x72
													0x54	0x41	0-27
															0-
															17
															0 ·
															12 0 ·
															0177 0 ·
															0862 0 ·
															1427 0 ·
															2676 0 ·
															3872 0 ·
															"5686 0 ·
															7676 0 ·
															9208
															Completely transparent
															end at, =
															474.

1) Find a list of such light filters. himself in Eder: «Ausführliches Handbuch der Photography », Vol. III,

5th edition, 1903, pag. 194 and 698, also in the "Yearbook of Photography and Reproduction Technology", 1900 to 1903.

2) Disc types that need less powerful correction filters would undoubtedly be better; one will have to strive for such better plates, although at present the erythrosine plates can hardly be dispensed with. •

3) Janusgr G of the color works Meister, Lucius and Br n in g in Hst a. M. According to the factory's reports, the same is an azo dye made from diethylsafranine and  $\beta$ -naphthylamine. I mixed 100 cm<sup>3</sup> water, 10 cm<sup>3</sup> Janusgrlung (1: 1000) and 10 cm<sup>3</sup> auramine (1: 1000) and used the color filter in 1 cm thick layers.

4) Recommended as a yellow filter by Andresen: «Photographische Correspondenz», 1898, p. 507.

5) Eder: "Yearbook for Photography and Reproduction Technology", 1901, p. 21 ~.

longer exposures than the light filters with new patent blue that I later found (Fig. 6, No. 5) and this is why the auramine decomposes by itself both in the light and in the dark by causing an immense yellow crystalline precipitate to fall 1). Incidentally, this filter results in the extreme, hardly permissible cut-off from. Yellow gr.

As a result, the red print negatives are not covered enough in light yellow and make them too bluish in three-color printing. For these reasons I gave up this Janusgr light filter.

Another light filter, which Baron Hl recommended 2), consists of Acid mixed with K a l i u m b i r o m a t 3); it is quite bright and very useful for certain purposes where moderate attenuation in the yellow- green is required. This filter gives the lowest, in some cases still permissible, but hardly sufficient attenuation for the erythrosine plates, which are enormously sensitive in the yellowish green, next to the woman near the Höfe rian line D in the yellowish green. This light filter (1 cm thick) works well for some types of sensitive plates, which is why I mention it here. The attenuation in blue (next color) is a bit too far against blue-green. As this type of light filter is noteworthy, I give my measurement results of the quantitative absorption in the following table.

Filter made of 10 cm<sup>3</sup> acid gr (1: 10,000), 10 cm<sup>3</sup> potassium dichromate (1: 100), 25 cm<sup>3</sup> water.

Scala 1 1 wavelength 1 luminous intensity 1 extinction coefficient Scala wavelength luminous intensity extinction coefficient

7¼ to 7½ 655 to 645 0 · 27 0 · 569 10¼ to 10½ 553 to 546 0 · 92 0 · 036

7½ 7s ;, "645 635" 0 · 15 0 · 824 10½ 10¾ "546 539" 0 · 91 0 · 041

7¾ 8 "635 625" 0 · 05 1 · 301 10¾ 11 "539 533" 0'95 0 · 022

8 8¼ "625 616" 0 · 04 1 · 398 clear

8¼ 8½ "616 606" 0 · 19 0 · 721 12 to 12¼ 512 507 "0 · 63 0 · 201

8½ 8¾ "606 597" 0 · 24 0 · 620 12¼ 12½ "507 502" 0 · 47 0 · 328

8¾ 9 "597 589" 0x32 0x495 12½ 12¾ "502 497" 0x31 0x509

9 9¼ "589 581" 0 · 43 0 · 367 12¾ 13 "497 492" 0 · 19 0 · 721

9¼ 9½ "581 573" 0 · 55 0 · 260 13 13¼ "492 488" 0 · 15 0 · 824

9½ 9¾ "573 566" 0 · 72 0 · 143 13¼ 13½ "488 484" 0 · 09 1 · 046

9¾ 10 "566 559" 0 · 76 0 · 119 13½ 13¾ "484 480" 0 · 06 1-222

10 10¼ "559 553" 0 · 80 0 · 097 13¾ 14 "480 476" 0 · 02 1\_ · 699

F erythrosine plates, however, according to my experiments, a suitable green filter for three-color printing should attenuate the yellow green more and the blue green less than the acid light filter described above. I achieved this best with a mixture of ammonium picrate and Neu-Patentblau (Neu-Patentblau 4B from the paint factories formerly Fr. Bayer & Comp. in Elberfeld). Curves I, II, III, Fig. 6, No. 5, are the absorption curves of three different concentrations of the blue dye with an approximately constant concentration of the ammonium picrate.

The best Grfilter for erythrosine bathing plates (Schattera's erythrosine plates) was the mixture of 80 cm<sup>3</sup> water, 30 cm<sup>3</sup> ammonium picrate (1: 200) and 15 cm<sup>3</sup> new patent blue (1: 1000),

1) This observation moved me in the further course of my work on auramine lungs and instead use ammonium picrate to steam blue-violet. The table given in the text contains the extinction coefficients of an aqueous auramine lung (1: 15,000) which, in a 1 cm thick layer, emits a usable attenuation filter for blue-violet; the ammonium picrate can be used in an analogous manner and is dealt with in another table in the text.

2) Baron H 1: "The three-color photography with special consideration of the three-color printing and the photographic pigment images in natural colors", Halle a. S., W. Knapp, 1897.

3) The acid filter examined by me consisted of 10 cm<sup>3</sup> acid gel (1: 10,000), 10 cm<sup>3</sup> potassium dichromate

(1: 100) and 25 cm<sup>3</sup> of water; Layer thickness for photographic recordings 1 cm.

t

18 J. M. Edler.

whose absorption curve is shown in Fig. 6, No. 5 (1), and whose light extinction contains the following table. For orthochromatic plates, the maximum sensitivity of which does not gravitate so much towards yellow (for example Lumiere's yellow-sensitive plates, as they came on the market in 1891), the addition of patent blue must be reduced to 10 cm<sup>3</sup>. (No. 5, II), while Monobromofluorescein:

Fig. 6.

• • •

• • •

• • •

...

1 potassium dichromate 1: 100 n potassium dichromate 1: 1000

• • •

,.

, ..

0 · 2

1. Naphtho orange 1:

500"

"

§

"

:

E

0

"

~ "

.5 ~

: <

~

II. Ammonium blood chromate 200 g iu 1000 cmJ gel

1. Tolanroth 1: 1000 II ToJanroth t.4000

• • •

• • •

• • •

..,

1 AuramIn 1.15,000 · II. Auram1 n I, 800

L 80 cm · W · sa, 1 O 8 'harvest w.ant1t cn. e, cm3 Wasst,; 30 · Ammo111umpaaa11,  
200 GO · .-, mmonlump! kra1 YI200 30 "A.mmo n lumpllcr! I t, '200 15- · Neu.-Palenlb! a1t  
J: 100D 10 · Neu- Palentbla11 t.1000 6 "Nn-Pat1ntbla11 111000

Quantitative spectrophotometric testing of light filters.

Collodion plates need the least amount of blue added to the Grfilter (5 cm<sup>3</sup>) (No. 5, III); yes, this is often already too strong and one will sometimes do well, this

1 plates without a color filter (or with a water filter) to re-expose a little or to give the sensitive layer a small addition of an eosin dye. The attenuation of the blue-violet by the previously specified quantity of ammonium picrate is appropriate (see Fig. 6, No. 5). The following tables give the spectral analytical numerical characterization of the GR filters currently used by me exclusively in combination with erythrosine plates. [Addendum.

Fig. 7.

In 1903

were some

3 dyes belonging to the cyanine series

discovered well

Effect of the solar spectrum

on the «panchromatic»

Orthochrome T-plates.

atically »from the Fraunhofer line C in orange-red

4 Yellow, green continuous until blue and violet are sensitive (cf. E. V a l e n t i n : «The sensitization of some dyes of the cyanine group on silver bromide gelatin» 1). 7 shows the scheme of the sensitivity curve of a silver bromide gelatin plate sensitized with ethyl red or orthochrom T (bath

5

plate) with short, almost normal exposure; with longer exposure the sensitivity, especially in the case of orthochromic T, extends somewhat further to B into Roth. Filter III, Fig. 6, is the correct filter for emulsion plates which are sensitized with King's Orthochrom T or Miethe's Ethylroth (bath plates); it almost dark like that of the color table

gives chrome yellow so Gr. The light filter No. II, Fig. 6, pushes the chrome yellow back very strongly, even more so the filter No. III. These plates can also be used behind a naphthol orange filter (1: 500) for the production of blueprint clichés. However, better sensitivity in the real Roth would be desirable. For orthochromic T-plates, the exposure time f filter No. I is 1¼ times as long as f Grfilter III or: filter I: II: III = exposure as 1 · 5: 1 · 3: 1.]

1) cf. pag. 155, III. Part of these

treatises. Grfilter f erythrosine bathing

plates.

(80cm ~ water, 30cm<sup>3</sup> ammonium picrate [1: 200], 15cm<sup>3</sup> new patent blueB [1: 1000].)



Scala Wavelength Luminous intensity 1 1 1 Extinction

coefficient Note  $6\frac{1}{2}$  to  $6\frac{3}{4}$  717 to 705  $0 \cdot 84$   $0 \cdot 0757$  . This

filter gives the

$6\frac{3}{4}$  710 694  $0 \cdot 70$  " O . 1549 Chrome yellow on the color table is the same as Schweinfurter's [or the size is a little lighter than

$7\frac{1}{4}$  694 683  $0 \cdot 56$  "  $0 \cdot 2518$  yellow. lukewarm is pressed. The concentration of picric acid must not be increased,

$7\frac{1}{4}$   $7\frac{1}{2}$  683 672  $0 \cdot 38$  "  $7\frac{1}{2}$  710 / 4 672 662 O . 17 "  $0 \cdot 4202$   $0 \cdot 7696$  but 30 cm represent a limit value. Rather, the picric acid can be reduced to 25 cm. Should be with some records

$7\frac{1}{4}$  662 653  $0 \cdot 04$  " total absorption 1 . 3979 types if the yellow tint appear less opaque, the patent blue would have to be reduced to 10 cm, n3

11  $11\frac{1}{4}$  565 to 559  $0 \cdot 03$  " 1 . 5229

$11\frac{1}{4}$   $11\frac{1}{2}$  559 554  $0 \cdot 09$  " 1 . 0455

$11\frac{1}{2}$  11  $\frac{3}{4}$  554 549 O 15 " 0

8239 II "f. 12 549 B43  $0 \cdot 21$  "

"0x6778 12  $12\frac{1}{4}$  543 538

$0 \cdot 26$  "  $0 \cdot 5850$

$12\frac{1}{4}$   $12\frac{1}{2}$  538 534  $0 \cdot 32$  "  $0 \cdot 4949$

$12\frac{1}{2}$   $12\frac{3}{4}$  534 530  $0 \cdot 37$  "  $0 \cdot 4318$

$12\frac{3}{4}$  13 530 525  $0 \cdot 40$  "  $0 \cdot 3979$

13  $13\frac{1}{4}$  525 520  $0 \cdot 46$  "  $0 \cdot 3373$

$13\frac{1}{4}$   $13\frac{1}{2}$  520 516  $0 \cdot 58$  "  $0 \cdot 2366$

$13\frac{1}{2}$   $13\frac{3}{4}$  516 512  $0 \cdot 68$  "  $0 \cdot 1675$

13  $\frac{1}{4}$  14 512 508  $0 \cdot 78$  "  $0 \cdot 1079$

14  $14\frac{1}{4}$  508 504  $0 \cdot 80$  "  $0 \cdot 0969$

$14\frac{1}{4}$   $14\frac{1}{2}$  504 500  $0 \cdot 72$  "  $0 \cdot 1427$

$14\frac{1}{2}$  14  $\frac{1}{4}$  500 496  $0 \cdot 72$  "  $0 \cdot 1427$

14  $\frac{1}{4}$  15 496 492  $0 \cdot 62$  "  $0 \cdot 2076$

15  $15\frac{1}{4}$  492 489  $0 \cdot 58$  "  $0 \cdot 2366$

$15\frac{1}{4}$   $15\frac{1}{2}$  489 486  $0 \cdot 49$  "  $0 \cdot 3098$

$15\frac{1}{2}$   $15\frac{3}{4}$  486 483  $0 \cdot 36$  "  $0 \cdot 4437$

$15\frac{3}{4}$  16 483 481  $0 \cdot 27$  "  $0 \cdot 5686$

16 16¼ 481 476 o x 18 "" 0 x 7447

16¼ 16½ 476 473 0 · 08 "" 1 · 0969

This is followed by the absorption of the ammonium picrate in blue and violet (see there). Grfilter for Lumiere's yellow grit sensitive plates.

(85 cm<sup>3</sup> water, 30 cm<sup>3</sup> ammonium picrate [1: 200], 10 cm<sup>3</sup> new patent blue [1: 1000].)

Scale 1 wavelength Luminous intensity 1 1 1 Extinction coefficient Note

63 /. to 7,705 to 694 0 · 84 0 · 0757 Start of absorption

7 7¼ "694 683 0x70" 0x1549

7 '., 7½ "683 672 0x48" 0x3188

7½ 7 "., " 672 662 0x37 "0x4318

7 "., 8" 662 653 0x21 "0x6778

8 8¼ "653 644 0x04" total absorption 1-3979 Wide absorption band

10½ 10 "., " 577 to 571 0 02 1 6990

10 '., 11 "571 565 0x05" 1x3010

11 11¼ "565 559 o x 12" 0 x 9208

11¼ 11½ "559 554 O x 19" 0 x 7213

11½ 11 3, '., "554 549 0x26" 0x5850

1! '., 12" 549 543 0x30 "0x5229

12 12 '., "543 538 0x33" 0x4815

12¼ 12½ "538 534 0x38" 0x4202

12½ 12¼ "534 530 0 · 39" 0 · 4089

12 "., 13" 530 525 0x43 "0x3665

13 13¼ "525 520 0x54" 0x2676

20 j\_ M. Ed er.

Scala wavelength 1 light intensity extinction coefficient

Note 13¼ to 13½ 520 to 516 0 · 62 0 · 2076

13½ ,, 13¼ 516 512 "0 x 72 0 x 1427

$13\frac{1}{4}$  14 "512 508" 0 x 78 0 x 1079  
 14  $14\frac{1}{4}$  "508 504" 0x80 0x0969  
 $14\frac{1}{4}$   $14\frac{1}{2}$  "504 500" 0 x 86 0 x 0655 point of greatest permeability  
 $14\frac{1}{2}$   $14\frac{1}{4}$  "500 496" 0 x 74 0 x 1307  
 $14\frac{1}{4}$  15 "496 492" 0x54 0x2676  
 15  $15\frac{1}{4}$  "492 489" 0x42 0x3768  
 $15\frac{1}{4}$   $15\frac{1}{2}$  "489 486" 0 x 36 0 x 4437  
 $15\frac{1}{2}$   $15\frac{1}{4}$  "486 483" 0 x 27 0 x 5686  
 $15\frac{1}{4}$  "16 483 480" 0x20 0x6990  
 16  $16\frac{1}{4}$  "480 476" 0 x 14 0 x 8539  
 $16\frac{1}{4}$   $16\frac{1}{2}$  "476", 473 0 · 08 1 · 0969

This is followed by the absorption of the ammonium picrate (see there). Grfilter f monobromo fluoresceinocollodium.

(85 cm<sup>3</sup> water, 30 cm<sup>3</sup> ammonium picrate [1: 200], 5 cm<sup>3</sup> new patent blue B [1: 1000].) Extinction

Extinction

Scale 1

wavelength Light

intensity Scala

Wavelength 1 light

intensitycoefficient

coefficient

t1

1

$6\frac{3}{4}$  to 7 705 to 694 0 · 76 0 · 1192  $11\frac{1}{4}$  to  $11\frac{1}{2}$  559 to 554 0 · 44 0 · 3566

7 "7 $\frac{1}{4}$  694" 683 0 · 68 0 · 1675  $11\frac{1}{2}$  "11  $\frac{3}{4}$  554" 549 0 · 54 0 · 2676

7 $\frac{1}{4}$  "7 $\frac{1}{2}$  683" 672 0 · 60 0 · 2219  $11\frac{3}{4}$  "12 549" 543 0 · 64 0 · 1938

7 $\frac{1}{2}$  "7 $\frac{3}{4}$  672" 662 0 · 40 0 · 3979 12 "12 $\frac{1}{4}$  543" 538 0 · 74 0 · 1308

$7\frac{3}{4}$  "8 662" 653 0 · 36 0 · 4437  $12\frac{1}{4}$  "12 $\frac{1}{2}$  538" 534 0 · 82 0 · 0862  
 8 "8 $\frac{1}{4}$  653" 644 0 · 19 0 · 7213 121/0.;  $12\frac{3}{4}$  534 "530 0 · 88 0 · 0555  
 $8\frac{1}{4}$  "8 $\frac{1}{2}$  644" 635 0 · 02 1 · 6999 completely permeable  
 total absorption  $14\frac{1}{2}$  ,,  $14\frac{3}{4}$  500 to 496 0 · 82 0 · 0862  
 $9\frac{1}{4}$  10 ,, "10  $10\frac{1}{4}$  596 to 589 589 583" 0 · 04 0 · 12 1 · 3979 0 · 9208  $14\frac{1}{4}$  ,, 15 "15  $15\frac{1}{4}$  496"  
 492 "492 489  
 0 · 62 0 · 56 1 0 · 2076 0 · 2518  
 $10\frac{1}{4}$  "10 $\frac{1}{2}$  583" 577 0 · 19 0 · 7213  $15\frac{1}{4}$  "15 $\frac{1}{2}$  489" 486 0 · 42 0 · 3768  
 $10\frac{1}{2}$  "10 $\frac{3}{4}$  577" 571 0 · 28 0 · 5529  $15\frac{1}{2}$  "15 $\frac{3}{4}$  486" 483 0 · 39 0 · 4089  
 $10\frac{1}{4}$  "11 571" 565 0 x 33 0 x 4815  $15\frac{1}{4}$  "16 483" 481 0 x 29 0 x 5376  
 11 "11  $\frac{1}{4}$  565" 559 0 x 39 0 x 4089 16 "16 $\frac{1}{4}$  481" 476 0 x 21 0 x 6778

This is followed by blue absorption by picrate.

In these tables of quantitative light absorption, the attenuation in the blue-violet is not specifically mentioned, because in all three cases it is due to the ammonium picrate. The absorption of this aqueous ammonium picrate (1: 800) is given in numbers in the table below and is shown graphically in FIG. 6, No.5.

Ammonium picrate lung 1: 800. (90 cm<sup>3</sup> water, 30 cm<sup>3</sup> ammonium picrate [1:

200].) Scala Wavelength 1 Luminous intensity Extinctions<sup>1</sup> Comment

coefficient 1

$14\frac{1}{4}$  to 15 496 to 492 transparent 15 151 /., 492 489 0 · 84 ""  $15\frac{1}{4}$   $15\frac{1}{2}$  489 ,, 486 0 · 70 "15 $\frac{1}{2}$   
 $15\frac{1}{4}$  486

483 0 · 52" "15 $\frac{3}{4}$  16 483 480 0 · 41" "16  $16\frac{1}{4}$  480 476 0 · 25 ""  $16\frac{1}{4}$   $16\frac{1}{2}$  476 473 o · 14 "" end at  
 A = 471 ls

approximately in this concentration in the green filters, mixed with patent blue, before 0 · 0757;  
 can be used as the limit value of the absorption against blue can · 1549 be weaker, not 0 ·  
 2840 but stronger for three-color printing. If necessary, this filter can serve as a light filter f  
 bromosilver collodion 0 · 3872 with monobromo fluorescein. In most cases, however, it turned  
 out to be better to add a little blue to monobromo · 6021 fluorescent plates, 0 · 8539 for  
 example 85 c1na H2 0, 30 c1n3 ammonium picrate 1:

200, 5 cm<sup>3</sup> new patent blue 1: 1000

Spectroscopic investigation of the effect of bichromats as light filters.

I do not like to use potassium dichromates as components of light filters for the red printing  
 plate for three-color printing. I came to this view by studying the optical behavior more  
 closely caused by the

bichromate. One percent potassium dichromates attenuate the blue and bluegrass very strongly and with a fairly steep curve (see Fig. 6, No. 1, and the following table). Dilute

Potassium dichromate 1: 100.

(1 g in a total volume of 100

cm<sup>3</sup>.)

1

Extinction

n

Extinction

n

Scala

wavelength

Light intensity

Scala

wavelength

Light

intensity

coefficient

coefficient

1

11 to 11¼ 563 to 559 0 · 86 0 · 0655 121 /, to 12½ 538 to 534 0 · 41 0 · 3872

11¼ "11½ 559" 554 0 · 74 0 · 1308 12½ "12¾ 534" 530 0 · 31 0 · 5086

11½ "11¾ 554" 549 0 · 62 0 · 2076 12¾ "13 530" 527 0 · 23 0 · 6383

11¾ "12 549" 543 0 · 54 0 · 2676 13 "13¼ 527" 525 0 · 15 0 · 8239

12 "12¼ 543" 538 0 · 46 0 · 3373 13¼ "13½ 525" 516 0 · 05 1 · 30103

Potassium dichromate 1: 1000.

(1 g in a total volume of 1000 cm<sup>3</sup>.)

13¼ to 13½ 520 to 518 0 · 64 0 · 19382 15 to 15¼ 496 to 492 0 · 22 0 · 6576

13½ "13¾ 518" 516 0 · 56 0 · 2518 15¼, 15½ 492 "489 0 · 18 0 · 7447

13¾ "14 516" 512 0 · 48 0 · 3188 15½ "15¾ 489" 486 0 · 14 0 · 8539

14 "14¼ 512" 508 0x42 0x3768 15¾ "16 486" 483 0x12 0x9208

14¼ "14½ 508" 504 0 · 36 0 · 4437 16 "16¼ 483" 480 0 · 09 1 · 0455

14½ "14¾ 504" 500 0 · 30 0 · 5229 16¼ "16½ 480" 476 0 · 07 1 · 1549

14¾ "15 500" 496 0x26 0x5850

Potassium dichromates (1: 1000) give a gently increasing absorption curve from green to blue (see Fig. 6), dampen the blue-violet light when using erythrosine plates, so that you can use them to produce "color-correct", monochrome landscape photographs or other recordings (monochrome painting reproductions). This dichromating (1: 1000) is an example of a very good milder damping filter for orthochromatic erythrosine plates, in which the photographic effect of the blue and violet pigment colors must be dampened (corresponding to «light yellow» damping filters made of yellow glass), while dichromating 1: 100 dem corresponds to the dark yellow glass commonly used in orthochromatic photography, which represents an energetic attenuation filter f blue. Since these yellow light filters are probably «standards» f represent orthochromatic recordings with erythrosine plates, I divide both the quantitative measurements as well as a graphic representation of their absorption spectra (see Fig. 6, No. 1) with.

Very dark colored bichromate filters can be produced using ammonium bichromate, which is easily soluble in water, for example lungs of 200 g to 1 l. A light filter produced with such a concentrated dichromate suppresses the blue and violet from the beginning so sharply that it can be used as a selection filter in a 1 cm thick layer, and it can even be considered as an orange filter for three-colorprinting.

J. M. Ed c r.

This 20% ammonium dichromate in a 1 cm thick layer is, however, at the limit of usability as an orange filter, because it still lets through too much yellow and green. According to my previous experience (especially with red-sensitive wool black plates and for the printing ink Milori blue in the shade of plate I), light filters of this type are too very light orange in color; they should be more red-orange in color.

Ammonium dichromate 200 g in 1 l gel.

Scala wavelength 1 light intensity 1 extinction  
coefficient 10 to 10¼ 589 to 583 0 · 82 0 · 0862

10¼ 10½ "583 577" 0'70 o 1549

10½ JO¾ "577 571" 0x58 0x2366

10<sup>3</sup>/<sub>4</sub> 11 "571 565" 0x46 0x3373

11 11 <sup>1</sup>/<sub>4</sub> "565 559" 0x32 0x4949

11<sup>1</sup>/<sub>4</sub> 11<sup>1</sup>/<sub>2</sub> "559 554" 0 x 17 0 x 7696

11<sup>1</sup>/<sub>2</sub> 11 <sup>3</sup>/<sub>4</sub> "554 549" 0 · 03 1 · 5229

I found a correct, practically useful orange filter in naphthol orange lungs 1: 500 in a 1 cm thick layer; they give an absorption curve which begins in front of the Fraunhofer line D and ends behind it, as FIG.6, No. 2, shows and the following table specifies in more detail.

Naphthol Orange 1:

500.Scala

9<sup>1</sup>/<sub>4</sub> to

9<sup>1</sup>/<sub>2</sub> 9<sup>1</sup>/<sub>2</sub> ,,

9<sup>3</sup>/<sub>4</sub>

9-

10"

10

10<sup>1</sup>/<sub>4</sub>"

10<sup>1</sup>/<sub>4</sub>

10<sup>1</sup>/<sub>2</sub>"

10<sup>1</sup>/<sub>2</sub>

10<sup>3</sup>/<sub>4</sub>"

Wavelength                  luminous

intensity1

610 to 603 0x84

603 596 0 72

596 589 0 56

589 583 0x40

583 577 0 11

577 571 003

Extinction coefficient

0 0757 0 1427 0 2518 0 • 3979 0 '7696 1'5229

The naphthol orange I used was the "Orange II" brand from the Badische Anilin- und Sodafabrik (a tropaeoline, the sodium salt of sulfanilic acid-azo-: ~ -naphthol). Both in combination with wool black gelatine plates and with ethyl violet monobromofluorescein bromosilver collodion it always served me well in practically frozen three-color photography.

As a practically inferior, poorly working light filter for the blue print negative, let me add the tol to red h, which I initially tried many times in concentrations 1: 4000, but then gave up again because it attenuates the color spectrum too much next to D, i.e. the opposite error as which showed concentrated dichromating.

The concentriFirst tolan reddening (1: 1000 and stronger) gives rigens in a 1 cm thick layer of good red dark-chamber panes, which cut red light better than some types of red copper ruby glass, which is why I also called this dye, already requested by E. Valena<sup>1</sup>), for a detailed investigation underwent. The following table, as well as Fig. 6, No. 3, give my test results:

1) "Photographische Correspondenz", 1901,

p. 37. Tolanroth.

1: 4000 1: 1000

Scala wavelength Luminous intensity 1 1 Extinctions-coefficient Luminous intensity  
Extinctions-coefficient

7¾ to 8 8 8¼ "8¼ 8½" 8½ 8¾ "8S / 4 9" 635 to 625 625 616 "616 606" 606 "597 597 589" -0 • 30  
0 • 40 0 •  
28 0 • 09 -0 • 0969 0 • 3979 0 • 5529 1 • 0455 0 • 37 0 • 21 0 • 09 - 0 • 4318 0 • 6778 1 • 0455 -

All of these absorption curves are related to extinction coefficients and  $\lambda$ ,  $\lambda$ . The former are entered in FIGS. 5 and 6 from the value 0 to 1 • 0; this corresponds to light intensities of 100 to 10 ¼, which remain in place when the light passes through filters. Curves drawn in this way give the true image of the dominant spectral zone in the sense of my cutouts (see before), which comes into effect through these light filters. In the case of the copious exposure necessary in the practice of painting reproduction, the effects, however, extend up to about 5¼ light intensity (= 1 • 3 extinction coefficient) and then the effective spectral zones as a whole will be broadened. I have not plotted the values corresponding to these low light intensities in the curves, but have given them in the tables, since they can at least still play a role in applied photography.

Test photos of the color plate with color-sensitive plates and light filters for three-color printing.

If you photograph my normal color table (plate I) with ordinary silver bromide gelatine plates behind a violet filter or with wet iodobromo collodion, that is, behind a water filter, cinnabar and chrome yellow



should appear like black and Schweinfurtergr like dark gray and be photographically suppressed; the result of such negatives is the autotypical copy shown in Plate I, Fig. 1.

An approximately correct acting size sensitive plate with a corresponding filter gives an effect, as Fig. 3 in Plate I shows, where red and violet appear very depressed, ultramarine moderately subdued and the Schweinfurtergr appears somewhat lighter than the chrome yellow (for example erythrosine plate with patent blue + Picrate filter); if the latter are both equally bright, you can also count on usable three-color printing clichés (with some tutoring through retouching). If, however, when using erythrosine plates, the yellowish is not attenuated enough, but the ultramarine blue is too much, the result is an image of the color table as shown in FIG. 4 in plate I; The three-color printer cannot do much with this because it prints incorrectly.

A plate sensitive to red (more correctly sensitive to red, yellow and green) should, behind a good orange filter, give red, orange with yellow almost like white, but yellow and green like gray, gray and blue like black. A Roth filter or dark orange filter give the color table as shown in Fig. 2, Plate I.

The spectroscopic description of the reflection spectra of my normal colors, which I described in detail above, explains this behavior for the gene.

If the color-sensitive plates and filters pass this simple preliminary test satisfactorily, then one can count on usable three-color clichés, in which the retouching will intervene to improve, but never have to form the main thing, which unfortunately not in practice if the photomechanical process is poorly penetrated rarely occurs but should be avoided.

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If one compares these results, the empirically found better division of the spectrum into three zones, with the theoretically possible three systems of three-color filters, then it emerges that the system of three-division of the spectrum mentioned at the beginning corresponds best to me, according to which the zones are whole or almost butt against each other, while overlapping of the zones usually gave no precise color selection in three-color photography.

Use of the three-color negatives for photomechanical printing purposes.

With three-color printing one has to take care of the production of reversed negatives; they must be accurate in size (direct recordings of inverted negatives by means of an inverted prism or mirror with the objective or copying in contact using the known methods for the production of reversed negatives 1).

In the case of three-color precision, the correct adjustment of the aperture and the exposure time, as well as suitable aperture shape and correct aperture change must be observed. Even if these principles of the autotype are known as well, the essential connection between these factors and color photography has not been published in an authentic manner been.

It will therefore appear as an appreciable hint for the practice of the three-color autotype if I give these dates (using Voigtlander's apochromatic collinear and Steinheil's orthoscopes with a focus of 40 cm).

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The three-color print and scales included in Plates III to VII of this treatise were displayed on the k. k. Graphic teaching and research institute made in 1903 by means of the procedure described in detail below.

The direct three-color autotype with electric light is carried out on the k. k. Graphic teaching and research institute carried out as follows:

1. Yellow printing plate behind the water filter: Wet iodobromo collodion.

Pre-exposure on white paper: 40 seconds with  $f / 50$  round aperture 2). Exposure to the picture: 2 to 3 minutes with  $f / 25$  3) to  $f / 18$  4) round aperture.  $f / 12$  square diaphragm of the shape shown here: W 40 seconds.

II. Roth printing plate behind G filter.

Light filter: 30 cm<sup>3</sup> ammonium pickling (1: 200), 85 cm<sup>3</sup> water, 5 cm<sup>3</sup> new patent blueing

(1: 1000). Albert emulsion with monobromo fluorescein (see before). Pre-exposure on white paper: 30 seconds with  $f / 50$  round aperture. Image exposure: 2 minutes with  $f / 25$  round aperture.  $f / 18$ : square aperture: 1 minute. (If you wash harder, higher-contrast negatives, you have to do a third one)

Exposure with a square diaphragm, W  $f / 18$ , for example 20 seconds.)

1) Eder: «Comprehensive Handbook of Photography», III. Vol., 5th ed., P. 596. At present, the k. k. Graphic teaching and research institute Magnaliumspiegel used.

2) That means the diameter of the round diaphragm =  $1/50$  of the focus of the objective used.

3) With greater reduction to less than half.

4) With smaller reduction to the same size.

•

III. Blue printing plate behind orange filter.

Light filter: naphthol orange 1: 500. Recept for the plate sensitive to red: Collodione emulsion with ethyl violet and monobromo fluorescein (see above). Exposure time the same as the previous plate. Pre-exposure on white paper: 40 seconds,  $f / 50$ . Image exposure:  $1\frac{1}{2}$  to 2 minutes,  $f / 25$ ; square aperture w,  $f / 18$ , 50 seconds. The Collodione emulsion negatives are made with hydroquinone developer (Eder: Recepte and Tables,

5th edition, pag. 34), fixed with fixing soda, treated like normal autotype negatives, iodized with iodine- iodine-potassium solution to a yellow color and weakened with dilute cyan-potassium solution (the dots are reduced, blackening with 5% sodium sulfide solution) .

The finished and dry negatives are finally poured with  $5\frac{1}{4}$  gelatin and possibly even varnished.

These practical reports give a clear picture of how "the above-mentioned photochemical processes, which are precisely determined by spectral analysis, can be adapted to the three-color printing used. The investigation of the quantitative spectral absorption of the light filters, as I have just described, and the application of the photographic laws of blackening appear to me the only correct way to arrive at a scientifically precise, comparable knowledge of the function of color filters for photographic purposes.

Photographic objective for three-color print.

For three-color printing does not have the usual achromatism of photographic lenses. Since you are able to produce three negatives behind orange, green and blue-violet filters, you have to orientate yourself to the dominant group of rays, which is easily possible due to my frustrations. When taking pictures behind an orange filter, an objective correction in Roth for the characteristic lithium line  $A = 610$  or the hydrogen line  $H_\alpha = 656$  (this is the Fraunhofer line C) should be recommended.

The Fraunhofer B 1 and violet-like achromatism results from my previous delusions.

The intrinsic sensitivity of the silver bromide gelatine extends to the exposure time which, at the point of maximum effect, is sufficient to achieve photographic "blackening" = 2, as a broad band between blue and ultraviolet of approximately  $A = 460$  to  $425$  nm). In sunlight (with glass apparatus) and with abundant exposure, the band of blackening (that is, "blackening" = 1 · 5 to 2) lies from  $\lambda = 480$  to the beginning of the ultraviolet (HK), so that when calculating the objective achromatism for the optician can leave the photographic effect on silver bromide gelatine up, whether he for  $A = 450$  or  $440$ , even for the area from F ( $A = 486$ ) to KH ( $A = 396$  and  $393$ ) (for example for the Fraunhofer line G [ $A = 434$ ]; 2) or h [ $A = 410$ ]) achromatized. The latter, however, approaches the needs of reproduction photography with iodized silver collodion, the maximum effect of which is at  $\lambda = 437$  begins, at  $A = 423$  and  $410$  lasts (see Table II, Spectrum No. 16) and which is particularly suitable for line reproduction and autotype because of its favorable gradation and the clarity of the lines. For Ordinary achromatic photographic lenses, which almost always with bromine ~

1) cf. pag. 126, Part II of these treatises, where more precise information can be found.

2) The line G associated with hydrogen should not be confused with the neighboring Fraunhofer line G in the solar spectrum ( $\lambda = 4307$ ), which corresponds to an iron line.

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J. M. Eder.

silver gelatine plates are used, it would be pretty irrelevant whether the union width of the yellow Fraunhofer line D ( $\lambda = 589$ ) either with the blue hydrogen line G' = H (r) ( $A = 434$ ) or with the purple calcium line (Fraunhofer g, that is)  $\lambda = 423$  or h ( $A = 410$ ) is strictly calculated.

For the iodized silver Collodion method, which is particularly used in reproduction photography, the correction for the middle violet ray  $g$  ( $\lambda = 423$ ) would be more suitable; of course, the optical calculation of the objective is different in one or the other case.

The outstanding optical institutes do not base the calculation of photographic achromats and apochromats on the same rays, as can be seen from the following list, which I owe the friendly original communications from the opticians concerned.

Type of achromatism of the objective.

The objective is corrected for the rays

According to Steinheil (ordinary objective)

$D = 589$   $g$  ( $\text{Ca}$ )  $= 423$  „ „ (Objective for three-color printing)  $C = 656$   $F = 486$  „ „ (Objective for astrophotography)

$g = 423$   $A = 389$  „, Zeiss (ordinary objectives)

$D = 589$   $G'(\text{H}\beta) = 434$  Voigtländer-Harting! (Ordinary objectives)

$D = 589$   $G'(\text{H}\gamma) = 434$  Correcting only for chemical rays, as in astrophotography, is according to Voigtländer

$F = 486$   $G'(\text{H}\alpha) =$

$434$   $h$  ( $\text{H}\delta$ )  $= 410$

$F$ )

$f$

Apochromat-Harting (Voigtländer) ( $= 656 \sim = 486$ )  $\text{H}\beta$ )

Goerz, double anastigmat, series III ")

$D = 589$   $G' = 434$  Goerz, Series IV

(Apochromat 3)  $D = 589$   $G' = 434$

1) "Photographische Correspondenz", 1902, p. 281, 455, 522.

2) CP Goerz notes on this that his double anastigmat of the series III for  $D$  and  $G'$  is corrected in such a way that for the central zone a complete coincidence of the surfaces takes place, with a small undercorrection ( $F$  shorter than  $D$ ) for the central zone and one almost equal overcorrection for the edge zone.

3) The apochromatic series IV of Goerz double anastigmats is also corrected for  $D$  and  $G'$ , but the choice of glass is made in such a way that the rate of dispersion in the glasses is as proportional as possible. Even the best glasses, however, show a tertiary deviation (which is particularly noticeable in the Roth), on the other hand it is possible to find  $C$ , Find  $G'$  for this Goerz double

anastigmat to coincide.

For the graphic filters for three-color printing, the main effect will be represented by the green Fraunhofer line b<sub>1</sub> (magnesium  $\lambda = 517$ ) and the apochromats for three-color printing would also have to be corrected for this beam.

The opticians currently do not specifically determine for this large beam, but rather achromatize, for example, orange and blue and assume that the correction would then also be included.

For blue-violet filters or when using photographic preparations which are only sensitive to this type of radiation, the following considerations apply.

Since experience has shown that with the iodized silver collodion plate without a light filter one obtains practically completely usable part negatives for blue-violet, the achromatization for  $\lambda = 423$  chosen by Steinheil corresponds well to this purpose. This is namely the same length which corresponds to the center of the main effect of the practically usable violet filter for three-color photography and with which the maximum effect for three-color printing also corresponds when it is the printing plate for yellow. According to these prerequisites, apochromats for three-color printing should be corrected in such a way that they are achromatized for:

Orange Green purple

Fraunhofer line C ( $\lambda = 656$ ) possibly lithium  $\lambda = 610$  Fraunhofer line b<sub>1</sub> = magnesium),  $\lambda = 517$  Fraunhofer line! (= Calcium),  $\lambda = 423$

Unfortunately, the radiation area from  $\lambda = 656$  to  $423$ , which is particularly important in three-color photography, is too large to achieve total correction, even if glasses are used which allow the secondary spectrum to be reduced. So one will have to begin with the strict color correction of a narrowly delimited area (from orange to the blue line  $\lambda = 434$ ) for three-color printing. It is in the interest of the constructing optician that it should be determined by photochemical means how narrowly the spectral region can be chosen in order to produce natural colorations for the three-color print; according to my experiments, this district should at most and only if necessary, from orange at  $\lambda = 610$  to blue at  $\lambda = 434$ ; the district should be almost too narrow for such apochromatic constructions. If it is possible to extend the color correction further into red-orange up to  $\lambda = 656$  and on the other hand to purple at  $\lambda = 423$ , then the result corresponds perfectly to the photochemical requirements; In fact, however, the practice of three-color printing also requires a correction which only extends to light blue ( $\lambda = 486$ ). It is assumed that it is possible to evenly correct the deviation in red, green and blue in such apochromats.

The correction of the apochromats produced in practice should by no means be carried out uniformly by all opticians. I examined two excellent reproduction objectives (with the setting of each color midway between the axis and the edge) for their deviations from the setting on the yellow D-line. Both gave the same size of the deviations, but one was much worse in red than in purple, the other almost as much worse in purple than in red. The experimental investigation by means of a comparative production of photographic three-color prints shows that the latter objective (which was better in red, worse in violet) undoubtedly produced more precise three-color prints, the former (worse in red), however, a noticeable blurring of the three-color print (noticeable inaccurate fit of the blue printing plate) gave.

This result is not strange for those familiar with color printing technology, because the yellow printing plate (produced by the blue-violet rays) is printed at the bottom and serves more for the general coloring of the layer, while the blue printing plate (produced by orange-red rays) is the last, which The final printing plate delivers which, in the sense of the printing technician, not only delivers colored ducks, but also has to precise the design and character of the image. Therefore it matters little if the yellow plate is inferior in sharpness, if only the red and blue printing plates are sharp and fit well.

So while f the usual reproduction objectives (f the wet Collodion method) should best be corrected f the Fraunhofer lines D ( ), 589) and g ( ), 423), for apochromats the correction f the Fraunhofer lines C 'Fund G' f the practical conditions of three-color photograpbie; However, other points of view for the color correction of the reproduction objectives should result from my research.

As for ordinary dry-plate photography, it can be taken as an experimentally established fact that there is no substantial difference in the behavior of ordinary objectives, be it that they are achromatized for Fraunhofer lines D and G 'or D and h . So you get practically not very different objectives if you have one or

4 "

J. M. Eder, Spectral analytical studies of three-color photographic printing.

the other requirement is not strictly adhered to, because the skilful choice of types of glass with as much as possible a proportional rate of dispersion provides a balance and because the two bands of the spectral color sensitivity of our photographic preparations have minor differences in the type of correction of the photographic preparations in the usual photographic processes Not let the chromatic aberration come into its own.

From a photographic and chemical point of view, these results point to those rays of the spectrum which should be used as a basis for the correction of chromatic aberration of common achromatic objectives and the apochromats for three-color photography.

Plate I.

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Spectral analytical studies he three-color printing.

Chrome yellow madder lacquer Milori blue

Fig. 1. Bromosilver plate behind Fig. I · 2. Red orange-sensitive plate, methyl violet filter behind orange filter

CHROr; IGIELB GRON ULTRAMARINE

## METHYL VIOLET

Fig. 3. Erythrosine plate Fig. 4. Erythrosine plate behind a good green filter behind a small green filter

.A. n h an g.

The studies of three-color photography and the manufacture of liquid light filters set out in the previous paper were followed by others at the k. k. Graphic teaching and research institute in Vienna (1903) extended experiments with dry filters.

The starting point for this was that of Dr. E. Kig in the inking units vorm. Meister, Lucius & Bring in Hhst

a. M. chemically pure dyes, namely: crystal violet, methylene blue (chlorine-zinc-free), tartrazine, patentblue and filter red I.

For the production of the dry filters 1) one uses 1½ to 2 1n thick, as flat as possible mirror glass 2) which is carefully cleaned with diluted hydrochloric acid, then with ammonia and alcohol before pouring on the colored layer. The dye solution is poured on to a leveling frame that is exactly positioned horizontally. 7 c111.3 Lung are poured per 100 cmt of the plate surface. Dye lungs are produced with which gelatin lungs (8% hard gelatin in water) are stained. The following are the precise data with regard to the composition and concentration thereof, the result being light filters which correspond to the system described in the preceding paperthe liquid filter are tightly connected.

Violet filter.

3 g crystal violet)

1 g methylene blue (chlorine zinc free) 1 ~ in the

heat. 2 drops of acetic acid 100 cm<sup>3</sup> of distilled

water

J

6 cm<sup>3</sup> of this violet lung are added to 100 cm<sup>3</sup> of 8% gelatin, filtered through a preheated funnel andpoured onto the mirror pane.

Gfilter.

3 g of

tartrazineI

6 g patent blue> valid in the \ Värme. 330 cm<sup>3</sup> of distilled

waterJ

6 cm<sup>3</sup> of the largest dye solution is added to 100 cm<sup>3</sup> of 8% gelatin, filtered and poured onto the mirrorpane.

1) According to the information provided by Dr. r- :. Kig in Hhst a. M. ") Such mirror glass can be obtained from the Stein company in Munich.

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Appendix.

Rothfilter.

5 g Filterroth I (Dianilroth)) in the heat.

200 cm<sup>3</sup> of distilled water 5 cm<sup>3</sup> of the red dye solution is added to 100 cm<sup>3</sup> of the 8% gelatin solution, filtered and poured onto the mirror pane.

For three-color autotype using Collodion emulsion, the following glasses are suitable: 1. As a violet light filter: two violet discs, cemented layer against layer; 2. As a large light filter: a griddle and a colorless glass plate; 3. as an orange-red light filter: two orange slices, cemented.

Regarding the cementing of the filters, the following should be noted: After the mirror panes poured with colored gelatinous coating are dry, they are cemented with Canada balsam, which is in chloroform 1). After cementing, the colored plates are left in a horizontal position, weighted with light weights, for a day and then dried at 40 ° C. for one day in a spacious drying oven.

As far as the light-sensitive plates are concerned, a normal wet iodobromo collodion plate is used behind the violet filter, behind the green filter the bromosilver collodion (see page 11), which is colored with monobromofluorescence and sensitized in weak silver nitration (1: 500), is used, behind the orange silver filter which is colored with 10% ethyl violet (1: 500 alcohol); the colored Collodion can be kept for weeks. The plate is poured with the colored Collodion, but not sensitized with silver nitrate, but simply removed well with water before exposure. Treatment with pure water is advantageous because the negatives become clearer (less veil) than if one were sensitized with aqueous silver nitration. Hydroquinone potash is used as the developer (see page 11).

For three-color photography according to nature is very suitable Orthochrom T-plates, the King's Pinachrom, which gives a similar color sensitization curve as Orthochrom, but has far better Roth sensitivity (or Aethylroth plates or other similar sensitizers) in combination with the said light filters; However, the Grfilter can be cemented from two large glasses.

The preparation of the Orthochrom T-plates takes place in the following way:

Gelatin dry plates from Schattera in Vienna or Lumiere or Agfa plates are bathed in a sensitizing bath of 100 cm<sup>3</sup> water and 2 cm<sup>3</sup> dye solution (1 g Orthochrom T in 1000 cm<sup>3</sup> diluted alcohol). Bathing time: 2 to 3 minutes; then it is drained in a cup of water for the same time and the plate is dried in the dark.

Exposure conditions:

for example in sunny

landscapes if: ~ ~ -: ~ ~ ~ tl ~ ~:

he.

3

1 IJ.



f Orthochrome plates behind the dry photos in autumn.

-Roth filter 2¼

These exposure conditions change with the type of lighting. In strong foggy weather in November, for example, the exposure ratio of violet: Gr: Rothfilter = 2: 3: 1½-The plates are developed at the same time and then processed into three-color cliches or projection images in the known manner.

1) Canada balsam in chloroform is sold by E. Merk in Darmstadt.V.

## EXAMINATION OF INKS.

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For testing printing inks for  
lightfastness.Of

E. Valenta.

(• Österreichische Chemiker-Zeitung •, 1900, No. 11.)

The testing of printing inks for their lightfastness is usually carried out by rubbing the color in question with pure resin-free linseed varnish, printing on a white paper surface (wood pulp-free rag paper) and then exposing the printed surface to daylight.

K. H a z u r a 1), to whom we owe very valuable information about the color lakes made from tar dyes, recommends proceeding in the following way:.

The area printed with the color in question is covered with black paper in such a way that at first only a square of the upper left part of the area is exposed to the diffuse light. After a week a part of the lower

left surface is exposed, after a further week a square of the upper right surface and after three weeks a square of the lower right surface is exposed, so that the individual sections have one, two, three, and four Weven if they were exposed to the effects of light.

H azur a refers to color lacquers or other pigments which do not show any change even after four weeks of exposure in June, July and August, as "lightfast", those that can withstand two to three weeks, as "eh t" and such which fade after a few days as "fake".

This method is certainly sufficient for the ordinary purposes of the practitioner. If, however, more exact experiments are concerned, and more exact comparisons are to be made between the behavior of individual dyes, then it is probably desirable to have a method which permits numerical data to be destroyed with the aid of any reference sample serving as a standard of the dyes given by the light.

Since I urgently needed such a procedure (in order to carry out a work which deals with the study of the colored varnishes of various tar paints with regard to their usability as printing inks), I worked out what is described below and demonstrated its usability through experiments.

To carry out this process, the pigment color to be printed, if it is in a dry state, is rubbed with half to a quarter of the amount of pure linen varnish and with this pressure

1) "Photographische Correspondenz", 1898, p. 49a. From: Negotiations of the III. Congresses for Applied Chemistry, Vienna 1898.

E. Valenta.

color, as well as a piece of wood-dead rag with the comparison color rubbed in the same way printed on paper.

The printed areas are partly covered with black paper and at the same time with the exposed to diffuse daylight until the greater part of the comparison dye is bleached

is. If one correctly chooses the dye that serves as the standard, the other color will also become fabric has already been changed. If this does not happen, replace the bleached one

Standard sheet a fresh sheet, let the light act again, etc. and repeat the process until the dye to be printed has also been bleached accordingly.

The determination of the amount of color which was destroyed by the light from the dye quantum on the printed flea, which had an optical effect, is done by colorimetric means and for this I use a Stammer colorimeter supplied by Schmied and Haen s c h in Berlin. In this colorimeter, as is known, the change in the He of the colored liquid column occurs by raising and lowering a tube closed at the bottom by a glass plate, which is immersed in the comparison color in another cylinder.

For the purpose of penetrating the experiment, a cardboard frame is placed on the matte porcelain plate, which serves as a reflector in this apparatus and is located in an inclined position under both bars, in which two strips of paper of the same size can be attached side by side in such a way that the each of these reflected light is thrown into the corresponding tube of the apparatus.

One then pushes the printed part of the test strip not struck by light into that half of the frame which is under the observation tube filled with air, and a piece of unprinted paper into the other half of the frame, which is under the liquid tube of the apparatus a.

A dye solution is now prepared, the color of which corresponds to that of the test strip printed with dye, which is no problem with the large number of tar dyes available to us today (you can also mix two or three dye solutions until the one you want Effect is achieved) and this lung, which should be so diluted that color equality is only achieved with a layer about 50 to 80 mm high, into the cylinder determined for the dye solution, whereupon the He of the liquid layer is averaged by lifting the bar of the screw on the instrument until both halves of the image field appear equally colored in the ocular.

Now you read off, put the one that was exposed to the light in place of the printed, unchanged strip, adjust again to the color equality of both halves of the field of view of the oculares and read off again.

In this way two numbers are obtained; let us denote them with A and B. Since the amount of coloring principle contained in a dye solution is proportional to the thickness of the liquid layer, the He corresponds to that layer of liquid, which was able to bring about the same coloration of both halves of the visual field of the ocular when the stripe was not changed by the light, 100% Dye.

The amount of dye destroyed by the light results from the proportion: A: (A-B) = 100: x (A-B). 100

X = .....

A.

in percent of the original on the in Betreight coming area of existing dye. For example, in a series of tests that I have frozen through, f Met h y 1 eo s in extra (as

For the jump of printing inks. Lightfastness.

Lead lacquer deposited on barite and rubbed onto fir, nis with half its weight) found:

A =

80mm B

2 · 8 "

A-B 77 x 2mm

X = 7720: 80 = 96 x 5%

In contrast, the same dye applied to the paper without a binder (rubbed with water) resulted in: A 120 · 0

B 46 8

A-B 73 · 2

X = 7320: 120 = 61 ° lo

If a dye of high lightfastness is to be compared with one of poor lightfastness, two, three or more strips of the fake dye will have to be inserted one after the other before a noticeable change in the strip printed with the real dye can be seen.

Assuming the case that one finds the more lightfast dye that n percent of it has been destroyed by the light and f the three stripes p, q and r percent printed with the lightfast dye, the ratio of the lightfastness of the two colors results

If, for example, one finds for the more lightfast dye the loss during exposure = 35% and with three strips of the paper printed with the lightfast color varnish exposed one after the other during the time of the light effect, the dye losses are 80, 86, 98%

that is, the first dye is 7 x 5 times more resistant to exposure than the second, which was used for comparison.

The printing ink is lightfast

1 num contains varnish loss on (varnish from

mer dye, solvent in percent A-B dye in methyl

violet on the color percent 2 B = 10

paint-related assumed)

1 Pa • anitriline varnish. 25 84-81 3 5 274 3

2 Azo yellow on Ba1'yum sulfate 25 66 58 12 · 1 79 · 3

3 Metanil yellow on barium sulfate 25 76 -64 15 8 60 8

4 Crocefoorange on barium sulfate 33 60-50 16 7 57 5

5 Orange T on barium sulfate 25 54-42 22 2 43 2

6 X11idine orange on barium sulfate 25 58 -42 27 5 34 9

7 methylene blue aut kaolin - 56-40 28 5 33 7

8 Alkali blue on barium sulfate 42 52-36 30 7 31 3

9 golden orange on barium sulfate 2fi R0 42 30 · 0 82 · 0

1\*

E. Va l e n t a, For testing printing inks for  
lightfastness.r '

The printing ink

Lightfastne

ss1

Loss at

contains

varnish1

(Paint

offNum

in percent

Dye

in

FRO

M

Dye, F 11 with t e

1Methyl violet

mer

on the color

Percen

t 2 B =

10

lacquer covered

accepted

) 67 5 -37

5

Lacquer orange on barium  
sulfate 25th

10

44 4 1 21 6

42

55-16

70 9

11

Victoria blue B on  
kaolin. 13 · 5

42

86-19

77 8

Victoria blue 4 B on  
kaolin 12 · 3

12

42

81-18

77 8

13 brilliant green on KaoJjn.

12 · 3

25th

Auramine O on

kaolin.52-8

14th

84 6

11 · 3

Malachite gr on

kaolin42

111-12

89 · 2

15th

10 · 8

42 109- · 6

94 · 5

16 methyl violet 8 B on kaolin

10 · 1

42 49-1 9

Methyl violet 2 B on kaolin

1796

10 · 0

1

As an example of the usefulness of the method for comparing the lightfastness of different colored lacquers, I would like to quote the table above, which shows the results of the investigation of a number by the company. Hamlet ter Meer in Ürdingen a. Rh. Contains printing inks made by the same company from tar dyes made available to the author.

Various colored varnishes from tar dyes as printing inks and as water colors are obtained via the V(Section I).

Of

E. Valenta.

("Österreichische Chemiker-Zeitung", 1901, No. 3 and 5.)

In number 11 of the "Österreichische Chemiker-Zeitung", III. Volume 1), I reported a colorimetric method for the quantitative determination of the dye destroyed by the action of light and air on papers printed with printing inks and the practical applicability of this method on a number of printing inks made from tar dyes, which the company «Weiler t er Meer »made available, explains 2).

In order to be able to get away from my plan, which is aimed at investigating the majority of those tar dyes which are used today for the production of colored varnishes for the purposes of colored paper, wallpaper production and primarily for those of book and illustration printing, an investigation is carried out in the I sent a request to a number of the most important paint factories of the Continent to supply me with the tar paint material which these factories actually supply to printing ink factories for these experiments for the purpose of producing varnish colors put. Almost all of them gave this request. The establishments in question 3) follow in the most amiable manner, so that I had ample material at my disposal for the planned experiments, for which I would like to take this opportunity to express my best thanks to the management of the inking units concerned.

It's a well-knownThe fact that the lightfastness of a lacquer color, apart from the dye itself used for its production, also depends on the type of precipitation, the precipitant (substrate) on which the dye is deposited, and also the binder for the dye, the ratio



1) cf. pag. 1 of these treatises.

2) The method also proved to be very useful in the further experiments made with it; it only fails if a greater change in color occurs during exposure. In order to be able to quantitatively determine the color loss in such cases as well, it is necessary to use spectrophotometric methods. I intend to use the spectrophotometer to print those dyes which, due to a large change in color during exposure, cannot be printed in the simple way indicated, after completing my work, and then I intend to be able to give quantitative information on these dyes too.

3) Actiengesellschaft f Anilinfabrikation, Berlin; Badische aniline and soda factories, Ludwigshafen a. Rh.

; Paint factories vorm. Ms. Bayer, Elberfeld; L. Cassella, Frankfurt a. M .; Durand, Huguenin & Comp., Geigy in Basel; Kalle & Comp., Bieberich a. Rh .; Farbwerk Mlheim, Meister, Lucius, Bring & Comp., Hhst

a. M .; Oehler in Offenbach; Societe chimiques des usines du Rhone, Lyons; Societe anonyme des matieres colorantes, St. Denis u. A.

E. Va 1 e n ta.

the amount of binder to that of the dye, the paper on which the color layer is applied and so on.

Therefore, in order to give my experiments practical value, I had to take these relationships into account and in order to bring clarity to this matter, not only had to produce the respective color lacquers myself from the dyes which I had been thrown into use, but also the production of the printing inks from the lacquers Pressure etc. awaken.

The production of the colored varnishes from the tar paint was in and of itself a lengthy and time-consuming work and this, as well as the fact that the exposure of the printed paper strips in the light can only be carried out in those seasons in which there are good lighting conditions, is the reason why Today I have examined only a fraction of the material put to me at my disposal, while a large number of colored lakes are to be examined this year.

Pure chemicals were used to precipitate the dyes. Precipitation and washing of the precipitates were carried out carefully, thereby avoiding the presence of harmful precipitating agents in the colored lacquers as much as possible.

The washing out of the precipitated colored lacquers was done initially by decanting, then on the filter with the help of the water air pump with distilled water. The paints were dried on absorbent paper at room temperature, then they were finely powdered and sieved through hair sieves.

The colored varnishes obtained in the manner described were rubbed very carefully on the coloredstone with that amount of varnish, which was necessary to achieve a full print.

The used varnish was a product completely free of all foreign additives, siccatives and the like, and made from pure flax by cooking. Gum water served as a binder for the watercolors.

As a base for the printing inks, a pure, completely wood-free rag paper (printing paper), as used for the production of valuable printing works, was used.

This paper is acid-free and chlorine-free and hardly changes color even after months of exposure, so it cannot have any influence on the printing ink or the water color applied.

The printing of the color on the paper was carried out very evenly from the stone using a lithographic press, so that the layer can always be assumed to be equally thick. The watercolor paint could not be printed on and was therefore applied with a brush and rubbed in.

For the purpose of a better overview of the results obtained, I have grouped the examined dyes according to the color of the printed strips. With the exception of the eosin varnishes and some other particularly lightfast colors, the lightfastness was determined on Alizar in red h 1 ac k from bluish, doughy (25¼) alizarin from the Badische Anilin- und Sodafabriken in Ludwigshafen a. Rh. " Manufactured according to the specification requested in the tables, the lightfastness of this lacquer = 1000 is assumed.

The first group of the investigated colors includes those dyes which produce red colored lacquer colors. Of the dyes used here, the eosin dyes have been compiled in a table (Nos. 1 to 9) because these dyes, as printing inks, rubbed with linen varnish, are characterized by a particularly low level of resistance to the action of light.

If we consider the numerical results contained in the tables, we must first and foremost They state that the colored lacquers, which are made from the dyes of the eosin group, rubbed with varnish, produce colors which do not differ from one another - particularly in that they are substantially more or less lightfast, but are rather equivalent in terms of their inauthenticity. The behavior of the eosin colored lacquers rubbed with water and rubber is much more favorable.

About the fading of different colored lacquers etc.

While the varnish colors were completely bleached after a 30-day exposure, the fleece colors had only suffered partial bleaching. Even a 24-hour exposure to sunlight and diffuse daylight in April would cause the strips printed with varnish to destroy 40 to 63¼ of the dye present on the printing area in question; the lead lacquers of these dyes are even more lightfast than the tin lacquers. These dyes are usually found on red lead, which is the substrate and colored red, and indeed lightfast, so that these colors only lose the fiery tone given to them by the eosin lacquer and the total fading of the printing inks in the light is prevented without the actual colors Color lakes of the eosin colors therefore become more lightfast.

In the second table (Nos. 10 to 25) the other red dyes which I have examined so far are compiled, which have been taken from various groups of tar dyes.

Table I.

E.

Valenta.

Table II.

Number

dye

Alizarin red, bluish 25¾, pasty bath. A.

S. Alizarin red, yellowish 25¾, pasty  
bath. A. S.precipitation

80 g dye 1 40 g soda I 2000 cm "water J 175 g sodium  
phosphate)> II2000 cm "water J 40 g Tkischroth)

> III

400 cm<sup>3</sup> water J

I, II and III poured together: A.

106 g of clay sulfate} I 2000 cm<sup>3</sup> water J 25 g calcium acetate) 250 cm<sup>3</sup> water fll 8 g tin  
chloride} 200cm<sup>3</sup> water J III

I, II and III cast together: B.

A was poured into B, boiled for 1

hourPrecipitation as in No. 10.

Color loss in

Ligh

tVer

, .\_\_\_\_\_ P\_ro\_c\_e\_n\_te\_n\_ \_J,

authenticityholds

nis

from

What

varnish

Varnish

ser

to

colou

r

colou

r

colou

$r^2 \cdot 3$

$1 \cdot 5$

7: 5

$2 \cdot 0$

$3 \cdot 0$

6: 5

I ....., f ..... ~ r ....., r ..... II ..... 1 --

13 a

Paranitraniline red

Excelsior, lacquer ponceau J N, Cassella

48 g paranitraniline (Cassella) 240 cm<sup>3</sup> water 114 cm<sup>3</sup> hydrochloric acid at 20 ° Be 24 5 g sodium nitrite(I)

50g β-naphthol 50 g sodium hydroxide solution at 40 ° Be 50 g soda

650 cm<sup>3</sup> of water 30 g of Tkischroth 2000 g of heavy spar powder (II) I well stuck in II, enter under Rren. 60 g aluminum sulfate, mixed with water

21 g of soda, precipitated, plus 15 g of dye and 10 g of barium chloride can be dissolved in water. 1: 2

6: 5

..... f ..... 4f ..... 1

13 b

Excelsior, lacquer ponceau J N,

Cassella 14th

Carmine      lacquer

No. 01

10 g of dye

1000 cm<sup>3</sup> water 250 g soda lung (17 1  $\frac{3}{4}$ ) 250 g chlorobaryum lung (21 6) 125 g chloromagnesia  
(13) 125  
g caustic soda (4 3)

9: 5

Precipitation

unknown 1 1: 1

8 o

18 6

14 0

12 · 0

15 · 8

15 "8

18 · 4

9 · 3

based on Alizarinroth =

1000 1000 750

-

188

107

annotation

Gives a very fiery varnish, which prints very well

Lacquer color, very fiery, somewhat yellowish red, prints very well

Very fiery, vermilion paint, prints well and  
evenly Fiery paint color, evenly bleaches  
without the tone to change

....., ~ .....

Fiery paint color,  
bleaches evenly without  
the color to change  
tone; prints fine<sup>95</sup>

81

Commercial product, best variety

About the behavior of different colored lacquers  
etc. Color loss in

Ver percent

light keeps it

real

nis from 1-- ~ - - -1 1 to Ali

Num

annotation

precipitation

ndye

What-tsarin

mer

F ~ :: s F ::; ~: -: a: ~ e ::;

b: -Color moved

80 g of dye 150 g of alumina

acetate Color lacquer, dark,

bluish ti

Bordeaux RL, 100 g soda

chiges red, changes the

color15th

3: 5

20 7 21 7

72

Cassella 400 g of chlorobaryum and the like

sound not, prints well and amount of water for the

lungevenly chemicals

..... If..... if..... <- 1..... -Very fiery

vermillion, Precipitation as in No. 12, only as a sub

16

bleaches evenly without

theParanitraniline red

1: 2 36 x 8

25th

60

strat instead of barite kaolin

Change tori; prints well ---, 1 ----- 11 ----- < ,

-1----- Precipitation as in No. 12, only instead

Fiery vermillion,

pale17th

Paranitraniline red barite calcium carbonate as sub1: 2

62 · 8

evenly, does not print

strictly 30th

50

Well

--- 111 ----- if -----; -1 ----- The paint received 1 part of the flax additive, as was the case with

Precipitation as in No. 13, but boiling Ponceau

3 RL, 18th

Printing hardens easily;

yellow 1: 2

38

39

heiss Berl. A.-G.

pithy red, becomes bluish in the light in the light

..... If ..... if .....; - 1 .....

60 g of dye 480 g of alum 115 g of

soda The violet-red paint is in the

Rhodamine B, 90 g tannin

Light red without

pausing 19th

1: 2

41 · 8

37 6

36

Bath. A. S.



darken

40 g of emetic tartar

Water for the lungs of the chemicals and the

dye 10 g of dye 20 g of clay sulfate

Very fiery red, prints a good

20 Ponceau R, 10 g soda

and retains the tone when using 34 g of chlorobaryum

3: 553 5 54 7

29

bleach at

Water for the lungs of the chemicals

Color lacquer, containing tin, unknown redwood

pigment 21

64 7

2: 3

20th

23

position regulation

Precipitation as in No. 19, only instead of

tannin Prints and is very bad

Rhodamine B,

sweat, to powder; precipitation

22 and Brechweinstein blood albumin and 1: 2 77 · 3 138 · 8

19 Bad. A. S. incomplete

Boiling the liquid

10 g of dye in 500 cm<sup>3</sup> of boiling water, apply 5 g of sodium acetate  
Very fiery red, evenly fades without that  
Scarlet fever G 00, 50 g of barite

Change tone; prints

fine.23 1: 2

17 x 5250 cm<sup>3</sup> basic alum (120 g

Oehler

Paint color, from the company

Alum, 1000 cm<sup>3</sup> water, soda

up to

placed at the beginning of precipitation) 150 cm • Chlorobaryum precipitation (24 • 4 ° / o)

..... f..... H..... - lf ...

> ---- 1 ---; ~

1-----1 10 g dye 500 cm<sup>3</sup> water

The paint color was made by Safranin

MO,5 g sodium acetate

Company manufactured by itself;

feu24

1: 2

16

red, turns purple in the

light 200 g

SchwerspatOehler with

brownish tinge

60 cm<sup>3</sup> of tartar emesis (1:10) 120 cm • Tannin (1:10)

at 60 ° Paint color, from the company

Scarlet 3 R 00,

25th

posed; very fiery

red, 15 6

Precipitation as in No. 22 1:

2 Oehler prints fine

E. Valenta.

As we can see from this compilation, among the red colors investigated so far, paranitraniline red, whose lightfastness is far behind that of alizarin red, but still surpasses that of carmine varnish, a pigment that is dearly paid for as a printing ink, is the next lightfast printing ink. But even with this dye there are great differences in the lightfastness, depending on whether the precipitation was carried out on barite, kaolin or lime. It seems best to deposit the dye on barium sulfate, although the kaolin varnish is more fiery. The lightfastness of the barite varnish compared to the kaolin and lime varnishes behaves like

19: 6: 5 and it seems as if the increasing alkalinity of the substrate would impair the lightfastness of the dye. I have also tried to replace the  $\beta$ -naphthol in the preparation instructions for paranitraniline red (No. 17) with corresponding amounts of resorcinol; orange-red, far less lightfast products are obtained. The loss of dye was 94 x 4 (varnish color), respectively 69 x 2 (water color) with the lacquer paint produced with calcium carbonate as substrate and the lightness: 15 x 8, compared to 50 when using  $\beta$ -naphthol.

So far, I have examined three samples of the "Ponceau" brands found on the market and it seems that the type of precipitation here has a particular influence on the lightfastness of the printing inks. The most lightfast colored varnish was obtained by the Excelsior-Lackponceau JN, namely the precipitation according to specification No. 13a, while No. 13b with the same dye gave a less lightfast varnish. The least lightfast varnish was produced by a "Ponceau R" (factory unknown), which was precipitated on barium sulfate and alumina hydrate. The behavior of the two rhodamine paints which were examined showed very different behavior. The dye fixed on clay with emetic tartar and tannin was far less sensitive to light than that precipitated with albumin by boiling on clay as substrate, and the color of the varnishes was also very different; While the first precipitation gave a violet-red lacquer which completely loses the violet tone in love, but is easy to powder and prints well, the albumin lacquer, in spite of its pure color, proved useless for graphic purposes, because it is difficult to powder and badly prints. With this varnish, too, the bluish tone turns into a pure red on exposure.

Table III.

Ver

holds

-

Number dye precipitation nis of

varnish to

colour

Loss of color in

percent Varnish dye

Water coloring

Light

really

on

Ali

czari

n

Note

blue red,

prickly,

= 1000

based

Anthracene blue

26SWX,

Bayer

Galletn

powder, 27

Bayer

Methilen blue

G, 28

Oehler

Precipitation as in No. 29. An excess of clay sulfate gives

bluer Te 50 g of dye 50 g of soda

5000 cm<sup>3</sup> water 300 g alum 250, g sodium phosphate in water gel 150 cm<sup>3</sup> calcium acetate (1: 10)

10 g dye in 1000 cm<sup>3</sup> water 5 g sodium acetate 200 g heavy spar powder 80 cm<sup>3</sup> tartar lump  
1: 10 160 cm<sup>3</sup> tannic lump (1: 10); like at 60 ° C.

1: 1

1: 1

1: 2 purple-tinged dark blue.

3 5 5 3

429

Prints fine

-, -, -

Dark purple. Prints very about the behavior of different color  
varnishes etc. 4 · 8 · 3 312 good and even

e-- -e ---

Color varnish, from the  
company 5 · 0 - 300 set. Light,  
pureBlue.

Prints fine.

Loss of color in light-

VerProcentenfastnessholds -, .\_\_\_\_,,

on Ali

embrace of

Num

Note Filling

Dye red, Wasmer Varnish Varnish Blue

s he

pungent, color

to the color

color

= 1000

based

60 g dye 120 g soda 20 l water

brilliant 300 g sodium phosphate

Nice deep blue.

Prints Alizarin blue

G, 1: 1

273

good, but must be very fine

powder, 10 g calcium acetate

291)

be rubbed

10 cm<sup>3</sup> Tkischroth, for cooking Bavarian

heated 800g alum, dissolved, added in water; cooked for

an hour 1.....lf.....1.....11.....11.....1

—! .....

10 g dye 1000 cm<sup>3</sup> water

Purple blue. The color lacquer

Wasserblau FE, prints well, the prints wer-

J

86 g alum

230 bath. A. S.

4: 5

30th

which is more bluish in the

light 28 g soda 7 g tin salt

..... 11..... il..... IJ..... H...

'..... 11..... 1

10 g dye 1000 cm<sup>3</sup> water, boiling 250 cm<sup>3</sup> soda lime (7 1  $\frac{3}{4}$ )

250 cm<sup>3</sup> chlorobarium solution (21

6 $\frac{1}{4}$ ) Something dull, dark blue. 31

Real blue 3

E, 8 · 0

14 0

4: 5

187

Prints fine

125 cm<sup>3</sup> magnesium chloride lung (13 $\frac{1}{4}$ )

125 cm<sup>3</sup> caustic soda solution (4 x 3 $\frac{1}{4}$ ) bath.

A. S. Add 100 g alumina hydrate in dough form

--1....., 1..... 11..... 11--

..... 11..... jf..... l

Precipitation as in No. 28, only instead

of on Sky blue color lacquer. 32

Methilen blue

G, t: 2

155

Prints fine

Barite on Kaolin Oehler

, \_C.....11.....11.....I ~ .....'- 1 ..... 11  
.....110 g dye

Natural blue, is called Fir10 g soda

nis color in the light bluusti water blue

FE, 117

eh. Precipitation with a tin bath. A.

S.20 g clay sulfate

12 · 8

33

4: 5

salt gave a more lightfast

one40 g chlorobaryum

Varnish 3 l of water

, \_Je -----\_ JI -----' ----- \_\_ jll --- H --- 1 ---- J '---- le -- Nice blue. Water alkaline blue 2 E,

color fiery, darkens in the

light12 · 8

117

4: 5

Precipitation as in No.

3034

something after, becomes bluish

tichiBerl. A.-G.

ger. Print! Well



, -1.....111.....1 ~.....jl.... l ..... H~ f .....

10 g dye 200 cm<sup>3</sup> water 20 g barite

Fiery, fiery blue, only darkens a little and alkaline

blue 7 E, 200 cm<sup>3</sup> Glauber's salt (14 2¼)

becomes more bluish in the

light, 30 7

49 Oehler

1: 2

35

then like with

prints fine. Color from the 200 cm<sup>3</sup> chlorine solution (244:

1000) Company made and 50 cm<sup>3</sup> of acetic acid

Violet paint,

fades, Acid Violet

4 E,

without changing the

tone. 47 9 91

31 bathroom. A.

S. 1: 2

Precipitation as in No.

20th 36

Water color more

fiery 6 g dye

The precipitation takes place

through 48 g alum

Boiling of the lungs; she is

37 Victoria blue E,

22nd

15 x 5 g soda

4: 5 an almost perfect one. The

Bath. A. S.

20 g albumin

The paint doesn't darken

much 1000 cm<sup>3</sup> of water

')} Another from Durand, Huguenin & Comp. related alizarin blue gave a dye loss of 5 x 70  
fo. Lightfastness = 264.2 \*

E. Va 1 e n t a.

Number Dye Precipitation Ratio of varnish to color Loss of color in percent. Light fastness on  
Alizarin red, bluish tint, = 1000 based on Note

Varnish color V \ cup color

38 Victoria blue B, bathroom. AS Precipitation as in No. 37, only instead of albumin tannin and  
tartar emetic 1: 1 96 5 ~ 97 6 --144 --171 , 166 15 5 Changes the color to a dirty gray-blue in  
the light . This  
occurs more strongly with oil paint

39 New ethylene blue N, Casse! La 6 g colorant 45 g alum 14 g soda 10 g tannin 1 g sodium  
acetal 1500 cm<sup>3</sup> water 1: 1 15 Precipitation complete. The color varnish becomes reddish with  
prolonged exposure. The water color is about as lightfast

40 Cyanol 3 G, Cassella 10 g dye were precipitated with 100 g lead acetate with appropriate  
amounts of soda and alumina sulfate 1: 2 10 Very fiery turquoise blue, bleaches evenly and  
completely

41 methyl violet BE, extra, bath. A. S. 5 g dye 108 g alum 35 g soda 7 · 5 g tannin 5 g emetic  
tartar 1500 cm<sup>3</sup> water 1: 1 86 8 · 6 Fiery colored varnish, bleaches evenly, becomes reddish in  
the process. The precipitation with albumin turns black-brown as a varnish color in the light

If we look at Table III (blue and violet dyes), we notice that it is the alizarin colors and anthracene colors, respectively, which are characterized by high lightfastness. Among these colors, the Brilliant alizarin blue should be noted, which provides a nice, well-printing, deep blue and is also very lightfast as a water color (see the table above).

Worth mentioning is the use of Methylene blue G. The two colored lacquers made with these dyes, which were made in the paint factory itself, showed very different behavior as varnish colors to the action of light. Here, too, it was found that precipitations on barite are far more lightfast than those on kaolin.

Table IV.

Color loss in light

Reverence for all percentages

hold

s1

alizarin

Number of

red, dye

precipitation

n

Annotation

Whatmer varnish

blue to

,

Ficracks, stain

= 1000

color

Naphthol yellow S,

Pure yellow, intense,  
prints Precipitation as in

No. 20

4 · 8

5 · 4

42 3123: 5 evenly bath. A. S.

-

15 g of dye

15 g soda diamine fast yellow

A, Orange yellow. Prints

50 g of

alum 4 · 8

3 · 3

43

312 Cassella

3: 5 very evenly

60 g chlorobaryum 1500 cm<sup>3</sup> water

About the behavior of different colored lacquers

etc. Loss of color light

Verin Procenten

authenticity holds

1 ----- ~ ---JlaufAli-Num

embrace of

precipitatio

nDye red,

annotation

Wasmer Varnish Varnish Blue

ser

pungent,

color for

coloring

= 1000

dye related

10 g dye 2000 cm<sup>3</sup> waterMikadogoldgelb 8 G, light yellow, becomes in

the light<sup>44</sup>

45 g of

alum1: 1

5 · 0

300

Mlheim

brownish. Prints a good 14 g of

soda<sup>48</sup> g of chlorobaryum

..... 1.....it.....1 ..... f.....11.....i,

1.....1

Golden yellow lacquer, changes the

Curcume "to,<sup>45</sup>

Precipitation as in No.

13 b3: 5

11 · 1

203

No hue of color in the  
light. Berl. A.-G.

Prints well and evenly

, -1..... 1t..... 11.....i ~

.....-1.....

Pure yellow, prints well, the whale  
yellow, 46

Precipitation as in No. 20 12 8

1: 1

117

The color tone does not change when fading Cassella

..... 1..... 11..... 11 ..... 1..... 1..... 1.....

10 g dye 100 cm<sup>3</sup> water 10 g sodium acetate

Color varnish from the factory

bezoMetanilgelb S,

25 g heavy spar powder called light yellow,  
changes the 47

16 7

1: 2

89

Almost no color tone. Prints pretty  
evenly Oehler 15 g Glauber's salt

60 cm<sup>3</sup> of water; at 60 ° precipitated with 35 g of chlorobaryum in 120 cm<sup>3</sup> of water

, -f.....11....., 1.....i>.....l.....i , -f.....1

Not suitable as printing ink Metanil Yellow S, 48

Precipitation as in No. 47, but on kaolin

1: 2 18 x 8 80 is the albumin precipitation of this Oehler dye

~ .....l.....ll.....ll.... 1.....1 .....-,, -1.....

10 g dye 500 cm<sup>3</sup> water 5 g sodium acetate color lacquer received from the  
factory 50 g heavy spar powder

49 Hydrazine yellow, Oehler 25 g basic alum solution (120 g 1: 2 20 · 1 75 th. Golden yellow,  
does not change the tone in the light. Prints

Alum, 1000 cc water, soda until

good at the beginning of the

precipitation) at 60 ° C. with

150 cm<sup>3</sup> chlorobaryum circulation (24 · 4¼)

..... 1.....it.....ir ...

~

f.....1

Changes the color of the  
Azoflavin S, Exposure, becomes  
brownish,

50

Precipitation as in No.

203: 5

20 · 4 10 · 3

73

Water color less than varnish

paint Bath. A. S.

, \_1.....11.....lt..... r- •

,t.....1.....1

Dye was mixed with alumina hydrate (from alizarin yellow

3 G, Changes colors in the light

51

Clay sulfate and soda), water 5: 6 23 6 26 6

63

clay, is cooked brownish and turkey

red powder

.....lr.....1 .....

t--

1.....1 .....t--

f.....1

10 g of dye

6 g sodium acetate Color: pure golden yellow,

will 360 cm<sup>3</sup> V .. 'ater Metanil yellow 000,

but in the light as a varnish

color 52

200 cm<sup>3</sup> Glauber's salt solution (1:10) was

1: 225th

60

brownish-tinged. printed colors! \ "e falls

with Oehler



varnish made by the factory 400 cm<sup>3</sup> chlorobaryum conversion (1:10) at 60 to 70 ° C.

..... t ..... il ..... 11 .....

—, —

f ..... 1

53

Mandarin G, extra, precipitation as in No. 13b

5: 3

64 · 5

58

23 Berl. A.-G.

E. Valent  
a.

Color loss  
in

Light ver

authenticity it holds

percenton A li

zari

n-

Num

nisvo

n

precipitation

Annotation

red dye water varnish

varnishblue to

ser

stitched, color

= 1000

color related

54 auramine, bath. A. S. 6 g dye 48 g alum 15 x 5 g soda g x g tannin 4 g tartar emetic 1500 cm<sup>3</sup> water 3: 5 77 x 3 138 x 8 19 light yellow. Prints well and bleaches very evenly without changing the color tone

- ---

55 Mandarin RL, Berl. A.-G. Precipitation as in No. 13 b 3: 5 84 · 5 64 18 Orange-red colored lake, darkens a little. Prints pretty much. borrowed well and evenly

The behavior of the different types of A 1 k a 1 i b 1 au is interesting. The colored lakes of these tar dyes, which are mixtures of the sodium salts of sulfonic acids of triphenylrosaniline and triphenylpararosaniline 1), give, when precipitated with tin salt on barite or only on alumina hydrate, more lightfast colored lakes than when the precipitation is carried out with chlorobaryum. Since these inks are a good substitute for ultramarine and are very suitable for the purposes of three-color printing, I made parallel experiments with two types of alkali blue (brand Rund B extra from the "Badische Anilin und Soda-Fabriken"), by using each of them Paint produced three colored lacquers according to the following regulations:

I. 17.5 g soda, 10 g dye in 250 cm<sup>3</sup> water, 54 g barium chloride in 250 cm<sup>3</sup> water,

. 16 g magnesium chloride in 125 cm<sup>3</sup> water and 5 x 4 g caustic soda in 125 cm<sup>3</sup> water. Precipitation perfect.

II. 10 g of dye in water, 72 g of aluminum sulfate in water, 35 g of soda in water, precipitated with tinsalt, containing 6 g tin salt.

III. 10 g of dye were gel in water with the addition of 5 g of soda and 120 g of barium sulfate, then the dye was precipitated with dilute hydrochloric acid.

The well-washed paints were vacuumed off and left to dry on absorbent paper.

The chlorobaryum precipitation resulted in "A 1 k a 1 i b 1 au B extra" a very pure ultramarine blue, which, rubbed with varnish, prints well, but darkens in the light.

The tin precipitation gave a splendid blue; The color of the varnish is reminiscent of gentian blossoms and has a lot of abundance, which prints well and hardly darkens in the light, while the hydrochloric acid precipitation produced a matt violet-blue varnish that was very lightfast but poorly printed.

The A 1 k a 1 i b 1 au R behaves analogously, only with this dye all the colored lakes are more violet-tinged. The lightfastness measurements made gave the following relative figures (loss of dye in percent with exposure of the same length):

I II

Alkali blue B extra 26¼

18¼ Alkali blue R 22%

18¼

1) G. S eh ultz: «Delicious organic dyes», 2nd edition, p. 88.

2) I chlorobaryum precipitation.

II tin precipitation. III hydrochloric acid precipitation.

About the behavior of different colored lacquers etc.

These experiments show that the tin precipitation with the alkali blue provides more lightfast paints than the chlorobaryum precipitation (in compliance with the described modalities), which also corresponds to the results requested in the table under nos. 34 and 35 with a different alkali blue and under different working modalities .

The tin precipitation has the advantage of giving very pure colored dyes which, as printing inks, do not darken or become yellowish.

The colored lakes made from water blue also showed a behavior similar to that of the alkali blue. For the purposes of chromo printing, lightfastness and printability are A 1 izar in blue, and bile in, methylene blue and alkali blue, respectively water blue, can be used well. Violet should be avoided wherever lightfastness is required. Methyl violet has the peculiarity that as a water color, similar to the color lakes of eosin dyes, it is significantly more lightfast than as a varnish color.

The yellow colors I have examined so far are listed in Table IV. Vvir see from this combination how extraordinarily different the lightfastness of these colors is.

The naphthol yellow S provides a very real yellow. In view of its lightfastness, the same appears to be a good substitute for chrome yellow, just like the different types of Mikado g e I b. The latter dye works just as well as the useful light yellow printing inks delivering,

adjoining the same dyes diamine real yellow and curcume "in, the group of Azo colors on.

Very pretty, but unfortunately very little lightfast colored varnishes are listed under nos. 54 to 57

Cold, well-printing color varnishes, of which the auramine color varnish, in conjunction with blue colors, has been used in practice for a long time to produce so-called «night green».

Table V.

Color loss in  
light Ver  
authenticity  
holds Percent on  
Ali czarin

Num  
nis  
from  
red,

precipitatio  
nannotation

Dye Was-Varnish Varnishmer

blue  
toser  
stitched, color  
= 1000  
color

5 g of dye were ge in  
water It, with a lung of  
Naphtolgr B, Dark green,  
yellowish tinge. 4 9  
3 • 5

40 g of lead acetate added and  
up to 2: 5

429 Cassella

56

Prints very evenly

Precipitation sodium hydroxide solution added 2 liters of  
water - r--

~

5 g of dye 30 g of alum

Coerulea, powder, dark size, prints 4 -4

4 6

1: 1

326 Bayer

57 25 g sodium phosphate moderate

10 cm<sup>3</sup> calcium acetate solution 1:50, boiled for one  
hour Caprigr, the dye doesn't get full

23 8

43 3 falls as in no. 39

6: 5

63

58

Mlheim come like

15 g of dye

1000 cm<sup>3</sup> of water Color becomes rapidly in

light 60 g of clay sulfate

Guyneagr,

B, 10 · 4

166

2: 5

144

yellowish and is very little Berl.

A.-G. 59 zl g of soda; fall with

best before 10 g chlorobaryum

in 1000 cm<sup>3</sup> of water

1

E. V a 1 e n t a, About the behavior of different colored lakes etc.

The large dyes investigated so far are listed in Table V, with the exception of some of them, which, like brilliant green, provide particularly light-resistant lacquers and which will be discussed later in the second batch of colors, the investigation of which will soon be started should.

The lead lacquer made from Na p h t o 1 gr proved to be extremely lightfast. This lacquer has a rich, dark-gray color and is very suitable as a printing ink, but also does not have nearly the same brilliance as the above-mentioned green colored lacquers from dyes of the triphenylmethane groups is mostly peculiar.

The Co e r u 1 e "in also gives a lightfast, less brilliant varnish with good printability, while Caprigr and the various Guyneagr deliver less lightfast, but very brilliant varnishes.

About the behavior of different colored lakes made from tar dyes as printing inks and as water colors (II. Section 1).

Of

E. Valenta.

("Österreichische Chemiker-Zeitung", 1902, No. 3.)

The following tables contain the results of testing a further number of dyes for the lightfastness and printability of the colored lacquers obtained from the same by means of different precipitation methods. The results obtained with an exposure lasting about four months (May to September) were related to alizarin red (light fastness = 1000), and also with regard to the test results published in the first paper under the heading "Dye loss in percent" with the test results To obtain comparable figures, the relevant figures were calculated on the dye loss of alizarin red =  $1 \cdot 5$  (respectively  $2 \cdot 3\frac{1}{4}$ ). (See tables below.)

The dyes contained in Table VI (red lakes) gave only less than satisfactory results, with the exception of "purpurine" and the "standard" alizarin red. The dyes "Janusroth" 2) and "Benzoechthroth", which provide varnishes that are somewhat more lightfast, are again characterized by the fact that these varnishes either do not print particularly well, as is the case with the former dyes, or have very matt colors while the dyes, which are not fast to light, give partly very brilliant colored lakes.

If one compares all the red colored lakes which I have examined so far with one another with regard to lightfastness, it turns out that the alizarin red is not achieved by any other red coloring matter. For most purposes, lightfast red lacquer colors can be described as paranitraniline red, precipitated on barite, in addition to purple, and lacquer ponceaux 3), which colors are also characterized by good printability, abundance and great brilliance.

1) cf. p. 5 of these treatises.

2) A new dye from Meister, Lucius, Bring & Comp., Presumably a disazo dye according to D. R.-P. 93.499 or 99.127.

3) See Table II on p. 8.

E. Valenta

Table

VI.

Nu

m

mer

59

60

61

62

63

64 65

66

67

68

dye

Alizarin red, bluish, 25 $\frac{3}{4}$ , bath.

A. S. Purpurin, bath. A. S.

Janusroth B, I \ I. L. B. & Co.

Benzoechoth L, Patent,

Bayer Azoroth B, Mlheim

Powder fox

Cochenilleroth, Bad. A.

S. Pyramin G, Mlheim

Brillant-Rhodulinroth,

Bayer Janus-Bordeau B,

M. L. B. &

Co.

precipitation

Cf. p. 8 of these treatises

10 g dye 16 g soda in 1000 cm<sup>3</sup> water 70 g sodium phosphate in 800 cm<sup>3</sup>

Water 16 ff Tkischroth 43 g of clay sulfate in 800 cm<sup>3</sup> of water 10 g of calcium acetate in 100 cm<sup>3</sup> of water

Boil 3 $\frac{1}{2}$  g of tin chloride in 40 cm<sup>3</sup> of water for 1

hour 12 g coloring 86 g alum 28 g soda 15 g

tannin

Boil 8 g tartar of water in a total of 3 l 1 g tin salt,  $\frac{1}{2}$

hour 10 g of dye

100 g clay dough 90 g barium sulfate 10 g barium

chloride Water in total 2 l

10 g of dye 31 g of alumina sulphate 14 g of soda 60 g of barium chloride water in a total of 3 l



Precipitation on clay with tannin and grape

tartarUnknown

10 g dye 200 g barite 10 g soda, neutralize with acetic acid 10 g tannin water in a total of 3 l 12 g coloring 86 g alum 28 g soda 15 g tannin

8 g of emetic tartar / Vasser in a total of

3 IAs with No. 67

Ratio of

Varnish to

color7: 5

6: 5

5: 5

3: 8

3: 6

4: 6

2: 4

2: 5

1: 1

1: 1

Loss of color in percent

Light-[

Varnish What authenticity (oil

note color ser color color)

1000 standard color, light fastness =. 1000

assumed Very fiery, somewhat bluish

326 former Roth. The color

prints prematurely

-

10 · 2

~~

11 ·

2

10 · 4

17th

Must be very fine if the color is to print

well147

be rubbed. Does not change the color tone in the light

Prints well, evenly bleaches moderately, but is not a fiery dye

Fairly strong red, yellowish tinge, does not print completely evenly. Changes the color shade only slightly in the light

Changes the hue in the light

17 · 2 14 87 something in dirty

purpleSpends little. Pale red.

22 · 9 21 · 8 65 Does not change the hue

in theLight

Spends a little with varnish

62 rich printing ink. Becomes yellowish in the light.

Printspretty good

Magnificent fiery red,

prints well, bleaches without

we 61 significant change in

the Evenly colored tones

Prints pretty well, extensively.

27 · 1 27 · 3 55 Dark red, violet-tinged,

It changes the tone to yellow-red when bleached

About the behavior of different colored lacquers etc.

1 number dye 1 precipitation color loss in percentage ratio of what-varnish varnish to color color  
color 1 light fastness (oil color) note

69 Tronaroth 3B, Bayer 12 g coloring 80 g alum 28 g soda 15 g barium chlorid 2 liters of  
water. Precipitation perfect 3: 5 28 · 7 25 · 3 52 Scarlet red, bleaches evenly, prints well,  
changes the colorshade only slightly to yellow

- ~

70 Rosindulin red 2 G, Kalle & Co. 10 g dye 215 g alum 70 g soda 12 g tannin 3: 5 29 · 2 25 ·  
2 51 Sches, yellow tinged red, extensive, prints pretty well. Changes the shade of color in  
love, becomes more yellowish

6 g of tartar emetic, at 40 ° C. felling

With regard to Table VII, containing blue and violet dyes, it should be noted that among the tar  
dyes mentioned here there are some which, as far as richness, brilliance and lightfastness are  
concerned, leave nothing to be washed off. This is where the Cr es s y 1b 1au 2 BS from the  
Mlheim paintworks goes, the methylene blue BB from the paint factories vorm. Beyer & Co. in  
Elberfeld, the alizarin cyanine 3 R, powder (dark purple, very extensive printing ink), the less  
fiery, black-blue printing inks supplying benzoin chtb 1au B (all from the latter company),  
furthermore the pure b 1au II from Baden aniline -and Sodafabriken, which delivers a nice,  
brilliantly printing blue, and the tar paints, which are not very brilliant, but produce fairly  
extensive printing inks: Naphtamine blue (Kalle & Comp.), Nil blue R (Badische Anilin- und  
Sodafabriken), Chicago blue R (Stock Corporation f aniline manufacture), Jan us blau R  
(Meister, Lucius, Bring & Comp.), Co ngoehtb 1au (stock corporation f aniline manufacture).  
With regard to the fast benzene blue B it should be noted that the precipitations with barium  
chloride produce colors that are much more lightfast than those with tin salt.

Here, too, it can be seen that the most brilliant colors in particular deliver colored lacquers,  
which are far too lightfast to wash. The splendid "turquoise blue", the patent blue, pure diamine  
blue, give very little light-fast colored lacquers, some of which still have the unpleasant property  
of completely changing the color tone in the light. With regard to the form y 1v io l e tt, it should  
be noted that it produces just as hot, fiery lacquers as the methyl violet investigated and  
described in Table II of the first treatise, which, however, are more lightfast than those of the  
latter, although they are still In this regard, leave a lot to be washed.

T from e 11 e  
VII.

Color loss in II

1

Ver-Procenten light fastnessNum

nis from

annotatio

ndye

Falling

What (Ölmer varnish

Varnish

sercolour)

to

color color color

6 g colorant 100 g clay dough (equivalent to 45 g alum, 14 g soda)

Deep blue, good printing ink,

Cressylbau 2 ES, 100 cm 3 tannin solution 1: 10 and

profuse and fiery, in

the1 9

1 · 7 789

3: 5

Mlheim 10 cm "sodium acetate 1: 10 color very lightfast

Water to len the dye and the chemicals about 2 l. Precipitation

complete3 \*

E. Val en ta.

Nu

m

mer

72

73

..... 11..... 11..... j l..... II--

74

75

76

78

79

dye

Methylene Blue BE, Bayer

Alizarin-Cyanin 3 R, powder, •

Bayerprecipitation

6 g of dye 45 g of alum 14 g of soda

6 g tannin 3 g emetic tartar water approx. 1 x 5 l; felled warm, precipitation complete

According to the factory's printed instructions (l. Th., P. 25), precipitation is completely produced Benzoechtblau B, Bayer

Naphtamine blue 5 B, l {All &

Co. Pure blue II, l 3ad. A. S.

Nile blue R, bath. A. S.

Chicago Blue R, Berl.

A.-G.

r....., 11..... Janus blue

R, Precipitation as in No. 67M. L. B. &

Co.

..... 11..... II .....

Congo -real blue, A.-G. A.-F.

..... 11..... I

Benzoechtblau B,

Bayer

12 g of dye

86 g of

alum 28 g

of soda

35 g

chlorbarium

Color loss in

Ver

Perce

t holds

nis

from

Varnish

Varnishto

color

color3: 5

3

3: 5

3

12 g dye 86 g alum 28 g soda 15 g barium chloride water in a total of 2 l

10 g dye 86 g alum 28 g soda 20 g clay sulfate 10 g barium chloride water in a

total of 2 l 10 g dye 10 g soda 20 g clay sulfate 34 g chlorobaryum water in a total

of 2 l Precipitation as in No. 71. Precipitation full

come

16 g colorant 86 g alum 28 g soda 24 g chlorobaryum water · in

total 2 l 3: 5

4th

3: 5

5

3: 5

3: 5

3: 5

--1,

3: 5

.....j

2: 3

Water in total 2 l. Precipitation

completef.....~.....'IJ.....l

Precipitation, as done in No.

74,3: 5

only instead of 15g barium chloride 20.f tin salt, was an almost

complete one8 "4

V \

ras

ser

colou

r1 · 8

-

4th

3 ·

8

Lightfastness (oil

paint)500

500

annotation

Deep blue, profuse, quite fiery, prints well

andevenly, the Nu changes

ance almost not when exposing

Intense, extensive, dark blue-violet printing ink, prints well and evenly

..... 11.....1

469

375

300

288

258

242

Deep, almost black blue with a violet cast, prints well

Very dark, reddish blue, extensive, prints well and

evenlyNice, deep blue, prints well and evenly

Dark blue purple, prints well

Not particularly brilliant, dark blue-violet. Changes the color tone in the light by turning it

brownIf ....

Almost black

ouch, prints pretty

evenlyll.....If .....

179

~ -1-I-

-8 6

4 · 5

174

1

Dark blue-violet printing ink. Changes the color tone quite strongly in the lightHI

Color darker than no.74 (barium precipitation). Prints well and

evenlyAbout the behavior of different colored lacquers etc.

Color loss in



Percent holds-

Light num

1 nis of fastness

dye Annotation.,

precipitation

mer varnish varnish-was-

(oilto the color ser-color)

color color

Nice blue, but prints Urania blue, precipitation, as in No. 67, was

an unnot special and changes im

11 · 4

1322: 3

82

Light the shade in

perfect dirty violet dahl i. Bar.

..... ll ..... lf ..... 11 ...

..... ~ ..... 1

Trona -Violet B,

Bordeaurothe color Bayer

Precipitation, as in No. 74, almost

complete2: 3

98

83

..... 11 ..... lf ..... 11 .....

f .....

Dark purple, changes the oxamine violet

GR, Color tone in the light in one

Precipitation as in No.

862: 3

17 4 26 3 86

84

dirty red violet. Prints pretty well Friedrichsfeld

..... II ..... 11 ..... 11 --

~ ..... 1

Precipitation as in No. 67;

changed Uneven printing,

changes 85

Sulphonic acid blue R, but at the same time the color and gives a

1: 1

17 · 2 14 · 6 87

the color tone in the

LichteBayergray-violet paint

..... II ..... 11 ..... II ..... le.. I .....

~ ..... 1

14 g dye 80 g

barite 86 g of alum

Dirty violet, bleaches benzo-real

violet, 2: 3

21 7 21 69

86 evenly

28 g soda 30 g Baryumchlorid water in total 3 l

~ --- Dark purple, changes the color tone in the light to a

Bavarian Oxamine blue BF, precipitation as in No. 86

2: 3

22 6 20 4 67

dirty red tinged Via

Friedrichsfeld 87 lett um; prints

unevenly moderate

Water in total 2 l; incomplete

88 Formyl violet S, 4B, precipitation as in Cressyl blue No. 71 5: 5 28 · 5 25 · 4 53 Prints well, very violetfiery

Cassella

8 g of dye

64 g of

alum

21 g soda. Magnificent green-blue color;

New patent blue, 10 g of tannin in the light, the same goes

quickly 89 Bayer 5 g Brechweinsteiu 2: 3 24 · 3 47 in a gray-

blue; ver changes the tone completely

Precipitation, even after further tannin and tartaric additives

~ ..... If ..... - 11--

—, — f ..... 1 .....

2 g dye 60 g Glauber's salt turquoise

blue G, Changes with prolonged

exposure

108 g of chlorobaryum

90

2: 5

36 25

60

the color becomes gray-  
blueBayer

6 g of ammonia molybdenum water in a total of 2 l -6 g of dye

-

Changes the color tone for län

50 g chrome alum turquoise blue

BE, less exposure to light in a

15 g soda 3: 5 60

57 6 2fi

91

Dirty violet red; Water

bavarian 8 g of tannin

color turns gray-blue 4 g emetic

tartar -1

10 g dye 'diamine pure blue

FF, 200 g barite

Will be under the

action 3: 8 64 3 53 7

23 3

92

## Cassella

60 g of barium chloride of light with a reddish tinge 24 g of Glauber's salt · Precipitation complete

E. Valent a.

Number Dye Precipitation Ratio of varnish to color Loss of color in percent What varnish  
color colorLightfastness (oil color) Note -

93 94 Tkis blue G, Bayer Tkis blue G, Bayer 2 g dye 108 g chlorobaryum 60 g Glauber's salt 2 g  
tannin 1 g tartar 15 g coloring 130 g alum 42 g soda 12 g tannin 6 g tartar Precipitation almost  
complete 2: 5 4: 4 78

· 3 70 · 9 --98 40 19 15 Prints good; fiery color fiery blue-green; prints fine

Yellow dyes, the color lakes of which far surpass the usable yellow color lakes contained in  
Table IV 1) in terms of lightfastness, are the Mikado g e1b (Farbwerk Mlheim), whose color  
lakes have great brilliance, good printability and high lightfastness.

Table VIII.

Number Dye Precipitation Ratio of varnish to color Loss of color in percent what varnishes! ·  
Color colorlight-II fastness (oil color) Note

95 Mikado yellow 6 G, Mlheim II precipitation as in No. 63, Azoroth B 3: 6 1 1 · 8 0 · 7 833  
Particularlyfiery golden yellow. Prints well and is extensive

--96 Mikado yellow 2 G, Mlheim precipitation as in No. 63, Azoroth B3: 6 1 · 8 1 · 5 833 Red-  
tinged  
yellow, very vivid. Prints fine. Extensive

97 Mikadogelb G, Mlheim Precipitation as in No. 63, Azoroth B 3: 1 4 · 6 5 · 2 326 Red-tinged  
yellow, veryvivid, extensive. Prints fine

98 99 silk yellow B, Mlheim Janus yellow R, M. L. B. & Co. Precipitation as in No. Precipitation  
as in No. 63 67 --3: 6 9 · 7 10 · 2 -C · ~ 3: 5 10 · 4 16 · 5 155 144 Red-tinged yellow.  
Prints well; when exposed to  
the light does not change the hue of red-tinged yellow. Abundant, prints well, changes the  
color tonelittle or not at all

~

100 II II quinoline yellow, bath. A. S. 15 g colorant 15 g soda 30 g clay sulfate 51 g  
chlorobaryum water in total 3 I II 1: 1 11 · 1 11 135 lemon yellow color; when exposed to the  
light for a long time, takes a pale yellow color on I.

In contrast, the investigated and in table IX compiled large colorants either dull, less brilliant colored lakes, or the lakes are characterized by extraordinary brilliance and richness, but are then very sensitive to light; Among these latter paint colors there are some which also have the unpleasant property of being longer lasting

1) Compare page 1 of these treatises.

About the behavior of different colored lacquers etc.

To change the color tone completely. This is where, for example, Janusgr, Azingr and, above all, Diamantgr B, whose clay lacquer almost completely loses its splendid color in the light and takes on a dirty dark red-violet, almost blackish color.

Table IX.

Color loss

in Ver

Percent

keeps

light

Num

nis from

real hot

dye

Fä11 ung

annotatio

nWhat

mer (oil

Varnish

Varnishser

color color to color color

Alizarin-Viridin, With Sodium Phosphate, Thonerdesulfat

.I \ liattes, little extensive

patented, precipitated in dough and soda; boiling.

Gr; changes the color

tone101

3: 5

9 · 2

163

shape,

only a little when fading

Precipitation was

completeBayer

'f ..... f ..... - lf ..... ~

· -1 ..... 11 ..... 1

Stone size, unsightly

Benzogr G, precipitation as in No. 86

102

10 · 1

149

Colour. Will when

exposing8 · 2

3: 5

Bayer

gradually gray

f ..... 11 ..... 11 .....

..... 1 ..... lf ..... l

Alizarine cyanine

Dark, pretty

good103

gr,

Precipitation as specified by the factory 10 8 12 8

139

printing size Changes the

Bavarian3: 5

Color very little

..... ~ ..... ~ f ..... ~ 1 .....

1 ..... 1

Very dark green;

becomesJanusgr,

from light to

dark104

Precipitation as in No.

673: 5

11 · 5

130

3

M. L. Br. & Co.

Gray with grem stitches

aroundchanged

I ..... ~ f ..... 1 ..... 11 ...



---

1.....

Boiling on clay under the use of  
alizarin production of alum, sodium  
phosphate, Light water size;  
changes

105

3: 5

101

Cyanine tin salt and some turkey red, ge

the color has been falling a little

.... 11.....11 .....

---

e--

1 .....

10 g of dye 10 g of  
sodaNeptungr S,

Vivid blue gr;  
changes 20 g of  
clay sulfate 106

3: 5 32 x 8 30 x 0

46

the color tone in the case of  
failureBath. A. S.

20 g sodium phosphate

almost no water about 2 l. Incomplete

precipitation 1...11....., f.....~ l ...

e ---- 1 ---a ~

f.....1

Dark Gr; is

from

Azingri.in,

Light in greyish

gray107

3: 5

28 8 31 2

52

Precipitation as in No.

62Mlheim converted to the

water color

in a purple-tinged gray

l.....ll.....lf.....11--

-

~

f.....1

20 g coloring 62 g alumina sulphate acid gr

3 B, Fiery green, pale without

28 g of soda

108

3: 5

Change of color

tone<sup>24</sup>

Bayer

120 g of barium chloride. Doesn't fall  
fullout. Prints fine  
come, 10 g tannin, precipitation perfect

..... 11..... <1..... 1 ~

~

f..... 1

8 g of dye 66 g of  
alum Dark, very  
extensive Diamond  
size B, he

Grin; changes in  
light<sup>109</sup>

21 g of

soda<sup>3</sup>: 5

Bath. A.

S.100

Color and goes in

dirty, 15 g of tannin

dark red violet

he 7 g of emetic

tartar<sup>f</sup>-

r.....,....., f-

f ----- 1 86 g alum and 28 g soda

Fiery green, very

pale Real size CR,

er110

12 g dye, addition

of3: 5

100 easy and perfect

Bayer 100

28 g of barium chloride and 5 g of tin salt. Falls incompletely

To determine the «opacity» of printing

inks.Of

E. Valenta.

("Österreichische Chemiker-Zeitung", 1901, No. 32.)

The opacity of a color is understood to mean the property of the same to prevent the underlay on which the respective color is printed from showing through, to "cover up" the underlay. The opacity will therefore be all the greater, the thinner that color layer can be, under otherwise identical circumstances, which is necessary to prevent the underlay from showing through.

For the practitioner who deals with color printing and is therefore able to print several colors on top of one another, knowledge of the opacity of the printing inks is of importance that should not be underestimated; it is often a criterion for the purity and good quality of some colors and is therefore also of interest to manufacturers and paint dealers.

In any case, the opacity of a dye depends on several factors; The shape and size of the individual colored particles play a role here, as does the fact whether they are crystalline or amorphous, whether they have a smaller or greater opacity, etc. The fact is that, depending on the manner in which a paint is made, products of very different opacity can be obtained, as can be seen on the types of white lead

made by different methods, on types of soot, on cinnabar produced by wet and dry methods, and others. can constat. Regarding the relationship between volume weight and fineness on the one hand and the opacity of a color on the other Mierzinsky already put forward the following sentence: "The greater the fineness and the lower the specific gravity of one and the same type of paint, the greater the opacity" 1).

As for the methods of checking a color on its covering term as printing ink, they are as simple as inaccurate in the form recommended in various places. Usually the test is compared with a recognized pure color of the same kind, which is used as the "standard", either by determining which quantities of a "sighting color" (f light colors are used for this purpose bone black, f dark barite white) for a particular one Quantum of dye must be added in order to achieve the same intensity with the «standard» and the color to be printed, or a weighed amount of color is rubbed with a corresponding (weighed) amount of linen or linen varnish and applied to a painter's cardboard with a brush, that the ground is completely covered and nowhere shimmers through; one now measures the size

1) "Handbook of paint production •, 1898, pag. 198 and ff.

the area covered with the rubbed paint, resulting in the ratio of the opacity of the tested paint to that of the «standard» paint.

The former method is suitable for determining the opacity and tinting power, the latter gives an indication of the assessment of the opacity of a pigment color. As far as the accuracy of both methods is concerned, it leaves much to be desired. The first requires the use of the same "standard" and the same "sighting" paint if results are to be compared with one another, the second, however, is due to the application of the paint with a brush, although it is difficult to achieve the same layers across the board 'Results of dubious values, but even assuming that this error is avoided by applying the color by means of press printing, whereby very even layers are achieved, one has the inconvenience that if one print is not acceptable, one can use the second overprint have to wait until the first one has dried, etc., which means that a lot of time is lost and the process is hardly applicable to certain weakly opaque colors. I tried to remedy this latter problem by, instead of a black base, producing a scale from black to white made of various mixtures of zinc white and lamp soot, rubbed with equal amounts of linen varnish, and printed on white, wood pulp-free paper, and then closed it Prende color rubbed with linen varnish of a certain consistency in certain proportions, he printed the scale across, which can be done by means of lithography or letterpress (clay plate). In all cases, a single print is required and after drying you only have to determine the number of the scale that appears completely covered.

This method has the advantage that, once the scale has been established, the procedure is easy to carry out, and that it gives results that are easily comparable everywhere.

But the production of the scale is, since it comprises a fairly large number of gradations, a cumbersome, time-consuming work; I therefore tried to find another way of doing the task I had set myself, a method for determining the opacity of pigment colors, which does not have the above-mentioned defects, or only to a small extent.

After a little practice you can easily compare different intensities of the same color using a suitable colorimeter and appropriately colored liquids 1), I tried, with good success, to use the colorimeter to determine the opacity of printing inks.

The principle underlying the "colorimetric method for determining the opacity of printing inks" described below is as follows: If a printing ink is distributed evenly in a layer of a certain thickness on a black surface, which absorbs all light, If the thickness of the layer does not exceed a certain limit, the amount of colored light reflected by the unit of surface may be less than that which is reflected by the same amount of color distributed in layers of the same thickness on a white surface of the same size.

The greater the opacity of a color, the greater the amount of reflected color. Light (assuming the same circumstances) when using the black base compared to that with a white base, since the former swallows up all the light that penetrates to it, while it is reflected on the white base.

So it is only a matter of measuring the amounts of colored light reflected in both cases and one will be able to determine the opacity of any color by the proportional ratio of the two reflections to express controlled amounts of light.

1) cf. pag. 1 of these  
treatises.4th

”

26 E. Valent a, To determine the <opacity >of printing inks.

Practicing this procedure is very straightforward. The color to be printed is rubbed with a certain, always the same amount of thin varnish to form a printing ink and then a pure white and a piece of matt black paper are printed with benzene from the lithographic stone or a clay plate in the press.

Furthermore, the white porcelain plate of the colorimeter, which serves as a reflector, is placed horizontally and a piece of white paper is pushed into that half of the cardboard frame that is under the liquid tube, and a piece of paper with the same into the second half of the frame prenden color of printed paper. The liquid tube is now filled with a dye, the color of which matches that of the printing ink and the amount of dye that is required for both halves of the field of vision to appear equally strongly colored (apart from the brightness). Let us denote by W the number obtained as the average number of ten readings; this corresponds to the amount of colored light reflected from the printed, white surface. In place of the white sheet of paper printed with color, we now put a sheet of black paper printed with the same amount of the same color, and attenuate the brightness of the light reflected from the other half of the frame to such an extent that both fields appear equally bright and are on the same level Coloring of both halves of the face. We get a number, S, which corresponds to the amount of colored light that is reflected from the printed black surface.

The ratio S: W, expressed as a percentage of W, gives a measure of the opacity of the dye, provided that the same quantities of varnish of a certain viscosity and of the color to be printed are used in layers of the same thickness.

I will try to explain this with a few examples which have been taken out of the number of printing inks I examined using this method.

Z in n above the trade gave W = 54 mm, S = 21 mm; so the opacity corresponds to  $38 \cdot 9 \frac{1}{4}$

Chrome yellow gave  $W = 56\text{mm}$ ,  $S = 35 \times 2\text{mm}$ ; the opacity corresponds to  $62 \cdot 8\frac{1}{4}$ . Krapproth left  $W = 58 \times 6\text{mm}$ ,  $S = 1 \times 6\text{mm}$ ; the opacity corresponds to  $2 \cdot 7\frac{1}{4}$ .

The opacity of the three mentioned colors examined by me, chrome yellow, vermilion and madder, therefore behaves like  $62 \cdot 8 : 38 \cdot 9 : 2 \cdot 7$ , that is, the tested chrome yellow has a 1 x 6 times greater opacity than that Vermilion, and this one 14x4 times as large as the madder proth.

In comparison with «standards», the method gives independent numerical, positive results; it can be frozen easily and quickly if a press is available which allows the color to be evenly printed on the stone or the clay slab.

The error which, assuming the manual skill in using the roller, can arise when rolling in the printing plate with the relevant color on the different surfaces to be printed with the same color, appears, as I have created, for practical purposes as good as irrelevant. Since the thickness of the layer of paint, if one takes care to always distribute the same amount of paint on the same surface with the roller and only then to roll in the stone or the clay plate from which the printing is to be carried out, differs very little, this error is even with well-covering colors of no practical importance. If one wanted to make them completely harmless, one can easily determine with the help of the balance how much dye has been applied to surfaces of the same size on the paper in question and include this data in the calculation of the opacity.

About the behavior of different colored lakes made from tar dyes as printing inks and as water colors (III. Section 1). Of

E. Valenta.

("Österreichische Chemiker-Zeitung", 1903, No. 16.)

In continuation of my investigations on this subject described in these treatises, I exposed a further number of colored lacquers made of tar dyes to daylight for almost four months and determined the color loss by the action of light on the paper strips printed with varnish paint or coated with water color.

In order to enable a comparison with the color lacquers I had already examined, the result was the same as with these on Alizarinroth\_ (bluish tint, in dough form) from the Baden aniline and soda factories, whose lightfastness was the same. 1000 was assumed, related.

The results of these investigations are contained in the tables below. There we find, with nos. 111 and 112, designated two red dyes, which, if they are sufficiently finely distributed on the substrate in question, are splendidly colored and deliver a black.

These lacquers, rubbed with varnish, give good, printable colors of great brilliance. One of these dyes is the azophoric pink of the color works formerly Meister, Lucius and Bring in Höchst am Main. When coupled with  $\sim$ -naphthol, deposited on barium sulfate, the same gives a very extensive printing color of a somewhat yellowish, intense red. This color does not correspond to alizarin red in terms of light

fastness, but like No. 112 it is of such great light fastness that it equates to the best of the red lacquersthat I have already described 2) earlier.

The monoazo dye described under no.112 (from 2-amido-1-naphthylmethanesulfonic acid, diazotized and coupled with ~ -naphthol), deposited on barium sulfate, is distinguished (just like the colors of this type containing kaolin or calcium carbonate as a substrate) by great brilliance and The purity of the color and prints very well. When deposited on barium sulfate, this azo dye gives more lightfast printing inks than on kaolin.

1) cf. p. 5 and 17 of these

treatises.2) p. 1. c.

3) "Chemisches Centralblatt", 1902 (II), pag. 919 (patent of the Badische Anilin- und Sodafabriken). 4 \*

-E. Valenta.

Of the other red dyes available in the table, some were deposited on different substrates or on the same substrate with different precipitants.

In the case of safranin, which was treated in this way, it was found that the most lightfast of the safraninlacquers examined can be obtained by precipitation with tannin-tartar on barium sulfate.

In the case of naphtha min b 1au 3 B, the precipitation with barium chloride on barium sulfate was found to be more lightfast than the precipitations of this dye. The tin salt precipitation produced more vivid, but, apart from the low degree of lightfastness, also poorly printing inks.

Among the blue colors requested in the table we find a color of very high lightfastness and durability, which does not change the color tone in light; it is the new meta min b 1au from Mlheimer Farbwerke. As mentioned in the table, this dye is only slightly inferior to alizarin red in terms of lightfastness as a varnish color, and as a water color it surpasses alizarin red.

Unfortunately, the blue dyes used under 124, 125 and 126 change the shade of color as printing inks in the light, which also applies to No. 127 and 128, which are also difficult to rub. It should also be mentioned that among the examined colors there is a thiofluorescein dye, the Cy c1am in, which, as lead lacquer, showed a higher lightfastness to the eosin colors, so that it should appear indicated in many cases to use the thiofluoresce "in dyes" instead of the fluoresce "in dyes which correspond to the color tone and which are unusually poor in lightfastness.

Red and purple colors.

About the behavior of different colored lacquers etc.

Blue colors.



Loss of color in percent

Light num

relation to authenticity of

NotePrecipitation

Dye (varnish-was-varnish

Varnis

h

colour)

ser

for 1 color color

New metamine blue Dark black blue. Prints 2 · 4

7 · 8

How No. 120 has been

felled3: 2

935123

good ' --, \_ 10 g of dye

MIheim Graublau, changes at the Belieh

200 g clay dough

Naphthamine blue3

B,

the color turned into a natural 124 14 486

3: 2

1590 g barium sulfate kalle & Co.

Gray

6 g of chlorobaryum precipitation complete

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Abbreviations: S. a. Be. = Sensitizing effect on bromide silver collodion. -S. a. Bg. = Sensitizing effect on bromine silver gelatin. (The rich numbers indicate the part, the Arabic the page number.)

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